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IDENTIFICATION OF WEATHERED OIL FILMS
FOUND IN THE MARINE ENVIRONMENT

John W. Frankenfeld, et al

Exxon Research and Engineering Company
Linden, New Jersey

June 1974

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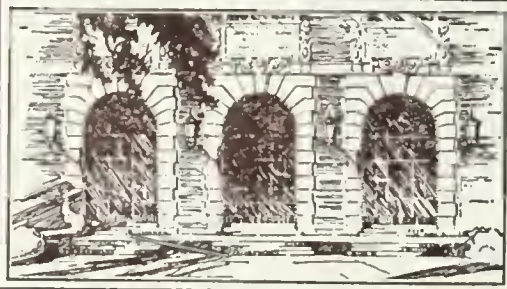
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16. Abstract A study was undertaken to develop a rapid, efficient method for identifying the source of spilled oil. Fifty-seven different petroleum products were weathered under controlled conditions in laboratory simulators. Samples were taken periodically and examined by a variety of analytical techniques. The analytical methods were graded on their abilities to (1) <u>classify</u> petroleum products as to generic type and (2) <u>identify</u> the actual source of the spilled oil. Four types of analyses were identified as being especially useful: thin-layer chromatography, infrared fingerprinting, gas chromatographic fingerprinting and liquid-liquid chromatography. The application of these techniques is discussed in detail and examples are given. By use of a combination of these four techniques all oils studied in this project could be uniquely identified.				10. Type of Report and Period Covered Final report. 15 June 1973 to 15 May 1974	
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LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BTU	British Thermal Units
cP	Centipoises
cSt	Centistokes
FBP	Final Boiling Point
GC	Gas Chromatography
GCD	Gas Chromatographic (simulated) Distillation
IBP	Initial Boiling Point
IR	Infrared
LC	Liquid Chromatography
PNA	Polynuclear Aromatic
RI	Refractive Index
SAE	Society of Automotive Engineers
Sp.G.	Specific Gravity
SUS	Saybolt Universal Seconds
TLC	Thin-Layer Chromatography
UV	Ultraviolet
VI	Viscosity Index

SUMMARY

A study was conducted to develop a rapid, efficient method for identifying the source of oil discharged into the marine environment. A set of criteria were established for evaluating potential fingerprinting methods. These were based on the U.S. Coast Guard's current needs and capabilities. Seven analytical methods were evaluated in light of these criteria. They were:

- Specific gravity determinations
- Gas chromatographic (GC) distillation
- Specific gravity/GC distillation ratios
- Infrared fingerprinting
- GC fingerprinting
- Thin-layer chromatography
- Liquid-liquid chromatography

Fifty-seven oils, representing the major classes of petroleum products, were obtained and artificially weathered in laboratory simulators for two weeks. Samples were withdrawn periodically and examined by means of the candidate analytical techniques. Judgements were made concerning the ability of the various methods to classify weathered oil as to its broad generic type and to identify the sample with an individual oil. That is, to discriminate among representatives of the same class.

No single method was found which could uniquely classify and identify all types of petroleum products. However, four methods were identified as useful components of an identification system:

- Thin-layer chromatography
- Liquid-liquid chromatography
- Infrared fingerprinting
- Gas chromatographic fingerprinting

The advantages and drawbacks of each method are discussed in this report. Examples are given which point out the characteristics of each and how these may be used in fingerprinting. These characteristics are discussed in light of the chemical composition of petroleum derivatives. Finally, several hypothetical classification-identification problems are examined which illustrate the integration of the chosen techniques into a successful fingerprinting system.

CONCLUSIONS

1. No single analytical technique can uniquely identify samples of all classes of petroleum products.

2. Of the seven methods investigated, the following have greatest promise as part of a classification-identification system.

- Thin-layer chromatography
- Liquid-liquid chromatography
- Gas chromatographic fingerprinting
- Infrared fingerprinting

2.1 Thin-layer methods are especially applicable to classification although they also have value in identifying certain types of petroleum products, notably lubricating oils.

2.2 Liquid-liquid chromatography, while in need of considerable development work, has potential for both classification and identification. Its greatest limitations, in the present form, are in classifying heavy residual fuels and lube oils and in the unpredictable effects of weathering. However, methods are available which should extend the scope of this method and overcome these difficulties.

2.3 GC fingerprinting is valuable for classifying and identifying samples. It is especially useful for identifying crudes and light refined products and has less application to heavy refined products such as lube oils and white oils.

2.4 Infrared fingerprinting is largely useful for identification. In the hands of an experienced person with an authentic sample, this is the most versatile tool for this purpose.

3. These four techniques, properly used in combination, are sufficient to identify, uniquely, all samples studied in this project.

4. For purposes of unique, unequivocal identification of a suspect source, an artificially weathered, authentic sample should be on hand.

RECOMMENDATIONS FOR ADDITIONAL RESEARCH

The major objective of the current research program has been to develop techniques, analytical procedures and methods for classifying a sample of spilled oil as to its general category of petroleum product. We have been able to do this using a combination thin-layer chromatography, gas chromatography, infrared spectroscopy and liquid chromatography. In addition to classifying oil samples, we have shown that these techniques can, in nearly all instances, uniquely establish the identity of the oil with an authentic sample. That is, to discriminate among samples within the broad categories. Nevertheless, additional work is needed to further develop, integrate and test the identification system and to tailor it more directly to Coast Guard needs. Continued research is recommended in the following areas.

1. Development of Liquid- Liquid Chromatography

Two major problems remain to be solved:

- The effects of weathering
- Reproducibility of analyses

This may be accomplished by:

- Artificially weathering authentic samples
- Examining heavy, weathering-independent components
 - Polynuclear aromatics (PNA's) by reversed-phase methods.
 - Removal of light ends by extraction or pre-chromatographing sample.
- Establishing standard procedures for conditioning columns.
- Running standard oils side-by-side with spill samples.

In addition, the scope of the LC method can be extended by:

- Using different columns and eluting solvents.
- Multiple elution.
- Using different types of detectors.
 - Variable wavelength UV.
 - Fluorescence.

It is recommended that additional research be carried out in all these areas.

2. Establish Usefulness of Current System by Additional "Challenges"

- Test some additional types of oils, among them:
 - (a) used lubricating oils
 - (b) ships bilge oils
- Test a number of "real world" samples. These could be "known" or "blind" and some could be samples of special interest to the Coast Guard.
- Weather some oils outdoors under various controlled conditions to determine the effects of environmental factors such as rain, sediment, microbial action, etc. on the analytical results.
- Determine sensitivity of the analytical methods to mixtures of oils and to the presence of extraneous, non-petroleum derived materials which may be picked up by floating oil.

3. Refine Techniques to Better Fit the Coast Guard's Needs

- Smaller samples
- Improved sample work-up
- Speed up analyses (if necessary and desirable)
- Further develop accelerated artificial weathering technique.

I. INTRODUCTION

A major problem facing any agency concerned with enforcement of oil pollution legislation is rapid identification of samples obtained in the field. Such identification is necessary to enable enforcement officers to obtain comparison samples from suspect pollution sources at the scene and to serve as a basis for later prosecution of guilty parties. The requirements for a workable system include the following:

- (1) Simplicity: require a minimum of special training.
- (2) Speed: analyses complete in a few hours at most.
- (3) Portability: adapted for use on board ship or in simple port facility.
- (4) Adaptable to very small samples: frequently only traces of a thin film will be available.
- (5) Accuracy and reproducibility: must discriminate among a large number of similar petroleum products with high degree of reliability.

In addition, the system must be independent of, or account for weathering factors.

The United States Coast Guard, as part of its Transportation Induced Pollution Surveillance System (TIPS), is concerned with developing just such a identification system as described above. This program was undertaken to develop a suitable analytical method or methods which would, as a minimum, allow a rapid classification of a pollution sample as to its broad product type. Hopefully, the technique would also provide sufficient information to make an actual identification of the sample with a suspected source. This report summarizes progress achieved toward these dual objectives. In the first section we will outline the characteristics of the important petroleum products which are necessary to their classification and identification and the analytical techniques which have been proposed for fingerprinting. This is followed, in subsequent sections, by an outline of the objectives and methodology of the program, experimental techniques and a discussion of the results and their interpretation. Finally, several examples are presented as to how the final, integrated system might function in identifying some hypothetical "pollution" samples.

I.1 Characteristics of Classes of Petroleum Products

Petroleum products may be broadly classified as:

- Crudes
- Residual fuels (Bunker)

- Blended residual fuels (low sulfur No. 6, No. 5, No. 4, or Navy Special)
- Distillate fuels (No. 2, Navy Distillate, Diesel, Kerosene - Jet Fuel, Gasoline)
- Lubricants
- Specialty products (white oils, solvents, greases and the like)

Such categories are useful in that they have easily distinguishable characteristics permitting reliable classification of a pollution sample. Frequently such classification will be sufficient to identify the source among several possible "suspects." Certainly it will greatly narrow the field and justify obtaining authentic samples from the remaining possibilities.

Petroleum products are extremely complex mixtures of hydrocarbons, compounds containing oxygen, nitrogen and sulfur and, in many instances, traces of metal salts. Some materials contain additives designed to impart special properties to the final formulation or to correct deficiencies in the base stocks which prevent the final product from meeting the necessary specifications. Because of this vast chemical complexity no two oils, even within the same classification, are exactly alike. Crude oils, for example, taken from the same field may differ widely in physical and chemical characteristics. These differences are reflected in the refined products obtained from these crudes. As a result, if the requisite analytical techniques are available, one can take advantage of such differences to uniquely identify a sample of spilled oil provided the origin and character of such differences are thoroughly understood and the effects of weathering can be predicted or otherwise accounted for(1).

Refined petroleum products are, for the most part, distillation fractions from crude oil which have been subjected to various purification and blending processes to obtain certain unique properties. The most important petroleum products from the standpoint of potential oil pollution include:

<u>Fraction</u>	<u>Approximate Boiling Range, °F</u>
Crude Oil	0-1050
Motor Gasoline	0-400
Diesel Fuel	350-720
Kerosene	325-525
Heating Oil (No. 2)	350-650
Residual Fuel Oil (Bunker Fuel)	600+

Within these broad classes a variety of other petroleum products are obtained by blending, extraction, use of additives and other petroleum processes. A summary of the major petroleum products and their gross characteristics is given in Table 1 (taken mostly from references 2, 3, and

Table 1

Characteristics of Petroleum Products*

Product	Boiling Range (°F)	Carbon No.		Uses	Other Characteristics
		Ave.	Range		
Motor Gasoline	0-400	C ₇	C ₄ -C ₁₂	Autos, trucks, marine	Numerous additives
Turbo Fuels	100-600	C ₈	C ₅ -C ₁₅	Jet aircraft	Branched paraffins, low mol. wt. aromatics, naphthenes with branched side chains
Diesel Fuels					
Automotive	325-650	C ₁₃	C ₉ -C ₂₁	Busses, trucks, tractors	Distillate fuels;
Railroad	350-675		C ₁₁ -C ₂₂	R.R. engines, marine engines	Paraffinic;
Marine	350-800		C ₁₁ -C ₂₄ ⁺	Heavy marine engines	Few additives
Fuel Oils					
No. 1	300-550		C ₈ -C ₁₆	Vaporizing pot burners	Distillate fuel
No. 2	325-645		C ₉ -C ₂₁	Home heating oil	Distillate; additives
No. 4				Industrial burners	Blended resid
No. 5				Industrial burners	Blended resid
No. 6				Preheated industrial burners	Blended resid
Lubricating Oils	650-1000		C ₂₂ ⁺	Engine lubrication	Branched paraffins and naphthenes; many additives
White Oils	650-1000		C ₂₂ ⁺	Medicinal oils	Highly refined, no aromatics

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* Taken from references (2-4).

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4, which contain much additional information). These characteristics and how they may be used to develop a classification-identification system are elaborated in the following subsections.

I.1.1 Crude Oils

Crudes are perhaps best characterized as having no definite characteristics. Except for additives, they contain all the chemical compounds of the refined products derived from them. They may be easily distinguished from other petroleum products by their smooth, continuous distribution of n-paraffins and other molecular types. This smooth distribution is quite obvious in gas chromatographic patterns, thin-layer chromatograms and the like (see Section IV to this report and ref. 1), and usually serve to classify crudes at a glance.* In addition, crude oils contain various nitrogen and sulfur compounds as well as bound metals. Crudes, however, differ widely in physical properties. They range in color from red-brown to black, may be quite fluid or semi-solid at room temperature and have densities ranging from 0.800 to 1.000(2).

Crudes vary even more in chemical characteristics although their average elemental analysis (Table 2) may be quite similar(2). Various methods have been proposed to classify crude oils. One such scheme, based on relative "paraffinic" or "naphthenic" character is given in Table 3. It is apparent that "paraffinic" crudes have lower specific gravities. Other schemes have been proposed and reviewed(5).

Table 2

Ultimate Analysis of Crude Oils, Wt. %

Carbon	83.9 - 86.8
Hydrogen	11.4 - 14.0
Sulfur	0.06 - 8.00
Nitrogen	0.11 - 1.70
Oxygen	0.5
Metals (Fe, V, Ni, etc.)	0.03

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* The single exception to this statement is that a heavily weathered crude will resemble an unblended residual fuel (Bunker).

Table 3

Classification of Crude Oils According
to the U.S. Bureau of Mines(1,2,3)

Class	Key fraction No. 1		Key fraction No. 2	
	Sp gr 60/60° F	° API	Sp gr 60/60° F	° API
Paraffinic	<0.825	≥40	<0.876	≥30
Paraffinic-Intermediate	<0.825	≥40	0.876-0.934	20-30
Intermediate-Paraffinic	0.825-0.860	33-40	<0.876	≥30
Intermediate	0.825-0.860	33-40	0.876-0.934	20-30
Intermediate-Naphthenic	0.825-0.860	33-40	>0.934	≤20
Naphthenic-Intermediate	>0.860	≤33	0.876-0.934	20-30
Naphthenic	>0.860	≤33	>0.934	≤20
Paraffinic-Naphthenic	<0.825	≥40	>0.934	≤20
Naphthenic-Paraffinic	>0.860	≤33	<0.876	≥30

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- (1) From Ref. (2).
 - (2) Key fraction 1 boils between 250 and 275°C; fraction 2 boils between 275 and 300°C.
 - (3)
$$^{\circ}\text{API} = \frac{141.5}{\text{SpG } 60/60^{\circ}\text{F}} - 131.5.$$

Crudes are sometimes classified by means of their API gravity and hydrocarbon content; Central and South American Crudes, especially Mexican and Venezuelan tend to be heavy (low gravity); Asian, e.g., Arabian, Iranian and Indonesian are of intermediate to high gravity and African (Libyan and Moroccan but not Egyptian) are generally light (high gravity)(2). European crudes tend to be of intermediate gravity while Canadian are medium to light(2). United States crudes run the gamut although most may be classified as medium to light. Other generalizations can sometimes be made. For example, younger, heavy crudes, such as Venezuelan have a relatively low hydrocarbon content and contain many heterocyclic sulfur and nitrogen compounds(3). Sulfur content, which may be dissolved or bound, ranges from about 0.03% for Pennsylvanian crudes to about 5.0% for Mexican. A high percentage of nitrogen compounds are found in Californian and, as already pointed out, in South American oils.

All these methods have serious drawbacks in that many crudes do not fit into any of the categories and must be classified as "intermediates" and exceptions to the generalizations are common. For our purposes it seems best to first classify a spill sample as "crude oil" (or residual oil) and identify it by comparison of its infrared or gas chromatographic pattern with that of an authentic sample.

I.1.2 Residual Fuels

Residual fuels of interest to this study are of five types:

- Straight run residuals (Bunker)
 - No. 4 oils
 - No. 5 oils
 - No. 6 oils
 - Navy Special fuel oil
- Blended resids {

The definition of a residual fuel(6) has traditionally been "that portion of the original oil that remains behind in the still and is withdrawn in liquid form." Thus, a true straight run residual fuel would simply be a crude oil with all components boiling below about 600°F removed. Such a material would be virtually indistinguishable from a heavily weathered crude. An authentic sample of a suspected source would be required. Most residual fuels, however, are blends of residual and distillate fractions. Blending is done for various reasons main among them the need to obtain a fuel with workable viscosity. Other goals of the blender would include consistency of product quality and the reduction of certain undesirable materials such as sulfur and sediment.

Because blending is usually performed with heavy residuum and a much lighter distillate fraction, blended residual fuels exhibit a clearly defined bimodal distribution of hydrocarbons. This shows up quite clearly in gas chromatographic patterns and serves to classify an unknown readily as a blended resid. Residual oils also contain the metals nickel and vanadium, present in crudes but largely absent in distillate fuels.

Residual fuels are classified by the American Society for Testing Materials (ASTM), into three grades on the basis of their commercial applications. These are summarized in Table 4. The special case of Navy Special fuel is covered in a separate subsection below. It is apparent that the distinguishing characteristic of residual fuels is viscosity; it is to meet this specification that is the main objective of blending. No. 4 fuels consist mostly of distillate fractions while No. 6 oils are largely residuum. Unfortunately this is a rather unreliable fingerprinting characteristic due both to weathering effects and the fact that a higher quality fuel may be sold in place of a less expensive one (i.e., a No. 4 or 5 as a "No. 6"). In addition, recent low sulfur requirements have necessitated blending many heavy oils with more light ends with concomitant decrease in viscosity(7). Thus, a No. 6 may be hard to distinguish from a No. 4 or No. 5 oil on the basis of physical properties alone. The effect of desulfurization on certain key properties of No. 6 oils is shown in Table 5. It is clear that this operation has a considerable influence on the characteristics of the products. As a result, classification as a blended residual fuel is safe but identification within the major category will usually require an authentic sample.

Table 4
Specifications for Residual Oils*

Grade of fuel oil	Flash point, °F	Pour point, °F	Water and sediment, % by volume	Carbon residue on 10 % bottoms, %	Ash, % by weight	Distillation temperatures, °F			Saybolt viscosity, sec				Kinematic viscosity, centistokes			
						10% point		90% point	Universal at 100°F		Furol at 122°F		At 100°F		At 122°F	
	Min	Max	Max	Max	Max	Max	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
No. 4 { Preheating not usually required for handling or burning }	130 or legal	20	0.50	0.10	125	45	(26.4)	(5.8)		
No. 5 (Light) { Preheating may be required depending on climate and equipment }	130 or legal	...	1.00	0.10	300	150	(65)	(32)		
No. 5 (Heavy) { Preheating may be required for burning and, in cold climates, may be required for handling }	130 or legal	...	1.00	0.10	750	350	(40)	(23)	(162)	(75)	(81)	(42)
No. 6 { Preheating required for burning and handling }	150	...	2.00	(9000)	(900)	300	45	(638)	(92)

* From Ref. (4).

Table 5
Typical Inspections for No. 6 Oils¹

Test	Method ²	Sulfur Content of No. 6 Oil (%)			
		0.3	0.5	1.0	2.0+
Ash (%)	AMS 80.01	0.01	0.017	0.04	0.07
BTU/Lb.	ASTM 240	19,292	19,304	19,067	18,671
Carbon (%)	Perkin-Elmer	88.07	87.11	87.94	86.25
Hydrogen (%)	Perkin-Elmer	12.01	11.85	11.23	11.81
Sulfur (%)	ASTM 2672	0.27	0.50	0.97	2.04
Con Carbon (%)	ASTM 189	0.50	2.43	5.64	12.51
Flash Point (°F)	ASTM 93	250	230	>220	158
API Gravity	ASTM 287	25.1	24.7	21.5	17.3
Nitrogen (%)	Kjeldahl	0.14	0.16	0.26	0.41
Pour Point (°F)	ASTM 97	+75	+35	+25	+5
Viscosity (ssu/100°F)	ASTM 88	167.9	224.9	586	3138

1. Refs. (6, 7).

2. See page iii for abbreviations used in this report.

I.1.3 Distillate Fuels

The distillate fuels employed in this study included:

- Automotive gasoline
- Jet aircraft fuel (Jet-A)
- Diesel fuels including marine fuels
- Light heating oils

I.1.3.1 Automotive Gasolines and Jet Fuels

These fuels are so volatile (final bp 400°F or less) that evaporation is virtually complete on all but catastrophic spills in a matter of hours. As a result we have not studied such products in great detail. These light materials may be readily identified by their IR and GC* traces. Gasolines have far more light aromatics than any other material we examined. Care is taken to exclude heavy aromatics which cause engine deposits. Jet fuels are much less aromatic and have a large percentage of paraffinic and naphthenic components. Branched paraffins are prevalent in both types. Typical hydrocarbon content of turbo fuels is given in Table 6. Aromatics content is limited to 20-25% by specifications. Average compositions of motor gasolines vary too widely to make tabulation useful. Here the important property is octane number. High octane values are achieved by blending in branched paraffins and aromatics and by use of additives.

Table 6

Hydrocarbon Distribution
in Turbo Fuels*

<u>Hydrocarbons</u>	<u>% by Volume</u>
Paraffins	33-61
Olefins	0.5-5
Naphthenes	10-45
Total Aromatics	12-25

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* Taken from Ref. (3).

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* See p. iii for abbreviations used in this report.

I.1.3.2 Diesel Fuels

Diesels are heavy enough to persist for some time and could present a serious pollution problem. These fuels have a boiling range of from 350°F to nearly 800°F depending on the grade. In this respect they are quite similar to light (No. 2) heating oils. However, there are other characteristics which help to distinguish them as a category.

Diesels are divided into four classes depending on usage. These are shown along with some typical properties in Table 7.

Table 7

Classes of Diesel Fuels(1)

	<u>Class 1</u>	<u>Class 2</u>	<u>Class 3</u>	<u>Class 4</u>
Cetane Number (2)	50	50	45	35
Boiling Range, °F	325-550	350-650	350-675	350-800 (90%)
Viscosity, SSU @ 100°F	33	35	36	50
Gravity, °API	40	37	34	23
Sulfur, Wt. %	.12	.30	.50	1.2
Uses	High Speed (>1000 RPM)	High Speed (>1000 RPM)	Medium Speed (500-1000 RPM)	Low Speed (up to 500 RPM)
	1. City Buses	1. Buses 2. Trucks 3. Tractors 4. Light Marine Engines	1. R.R. Engines 2. Marine Engines 3. Stationary Engines	1. Heavy Marine Engines 2. Large Stationary Engines

-
- (1) Typical average properties for East Coast, specifications vary with different regions.
- (2) Measure of "paraffinicity"; high numbers indicate performance approaching that of n-C₁₆.

Diesel engines are ignited by compression rather than spark as in gasoline engines. As a result, an important property of diesel fuel is its ignition quality under compression. In general, the more paraffinic a fuel the better its ignition quality. This is reflective in a high "cetane number" (Table 7). Diesel fuels, therefore, tend to be more paraffinic than other middle distillate fuels such as No. 2 heating oils. This distinction is noted in our analytical work and is discussed below. It must be stressed that this is a generalization only and in some cases the differences are slight.*

* Additionally, diesel engines are versatile and can run on a wide range of fuels, albeit inefficiently. Instances of diesel trucks running on heating oils are known.

Diesel fuels contain additives. These include:

- Stabilizers
- Cetane improvers
- Emulsion breakers
- Rust inhibitors
- Pour depressants

However, these are of fewer and of different character than those in motor gasoline, heating oils and lube oils.

I.1.3.3 Heating Oils

Two grades of heating oils are recognized; No. 2, the common home heating fuel, is by far the more prevalent. Grade No. 1 oil is kerosene, once the most important petroleum product but now representing only 1% of products based on crude oil (6) (not including kerosene-type turbo fuels). Typical specifications for No. 1 and 2 oils are given in Tables 8 and 9. No. 2 heating oils, like diesel fuels, are characterized by their narrow boiling range, exhibiting neither light nor heavy ends. Both GC and TLC methods may be used to classify these oils as distillate fuels. The boiling range of No. 2 heating oils is quite close to that of automotive diesels so other methods must be used to distinguish them. As pointed out in Subsection I.3.1, diesel fuels tend to be less aromatic than heating oils and contain fewer additives. Heating oils, in fact contain sizable amounts of polar additives:

- Flow improvers
- Viscosity modifiers
- Stabilizers
- Antioxidants
- Rust inhibitors
- Dispersants

As will be emphasized (Section IV below) the additives which may be present in up to 0.5%, can be detected and may be useful fingerprinting indices.

I.1.4 Lubricants

Lube oils are prepared by blending specially prepared base stocks and additives to suit certain specifications. The base stocks, from which lubes are derived, are obtained from the "bottoms" of atmospheric pressure distillation of crude oil. Thus, lubricants have average boiling points >650°F. The reduced crude is further distilled under vacuum to obtain several narrow boiling lube fractions as well as overhead fractions and a residuum. These are blended and further processed to give lubricants of the desired properties for various applications. The desirable properties for motor lubricants are oxidation stability, good color and, paramount in

Table 8

Typical Domestic Kerosene
(No. 1 Oil) Characteristics*

Gravity, °API	43
Distillation, °F	
IBP	330
50%	440
FBP	520
Smoke Point, mm	22
Wick Char, Mg/Kg	25
Sulfur, Wt. %	0.05
Color, Saybolt	22
Flash (Tag Closed Cup), °F	130
Viscosity, Kinematic, cs @ 100°F	1.4

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* Ref. (6).

Table 9

Typical No. 2
Heating Oil Characteristics*

Gravity, °API	34
Viscosity, Saybolt Seconds	
Universal @ 100°F	35
Distillation, °F	
IBP	325
50%	500
FBP	645
Carbon Residue on	
10% Bottoms, Wt. %	0.10
Pour Point, °F	-5
Flash (Pensky-Martin), °F	150
Color, Tag Robinson	14
Sulfur, Wt. %	0.40

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* Ref. (6).

importance, good viscosity index (VI). Generally, the most useful hydrocarbons are naphthenes and branched paraffins. Normal paraffins are too waxy, have too low a pour point and must be removed. Aromatics and olefins are unstable, have poor VI characteristics and are, therefore, undesirable. Asphaltenes must, of course, also be removed. These characteristics are reflected in the physical and chemical properties of lubes which help to distinguish them as a class (Section IV). A summary of properties of lubricants is given in Table 10.

Table 10
Properties and
Characteristics of Lubricating Oils

<u>Property</u>	<u>Desirable</u>
Hydrocarbon Type	Naphthenic, branched paraffins
Boiling Range	600-900°F
Viscosity Index ⁽¹⁾	High
Pour Point	Low
Cloud Point	Low
Color	Light
Oxidation Stability ⁽²⁾	High
Flash Point	High

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(1) Measure of resistance to change in viscosity with temperature.

(2) Aromatic and olefinic compounds are undesirable.

Lubricating oils for crankcases are classified according to their SAE (Society of Automotive Engineers) numbers which reflect the viscosities of the various oils at specific temperatures. The relationship between SAE numbers and viscosity is shown in Table 11.

In addition to crankcase oil, a variety of industrial lubricants are manufactured. These include⁽²⁾:

- Machine oils
- Steam cylinder oils
- Steam turbine oils
- Reduction gear oils
- Compressor oils
- Hydraulic fluids
- Motor bearing oils
- Spindle oils
- Cutting oils
- Instrument lubricants

Table 11

SAE Viscosity Numbers for Crankcase Oils⁽¹⁾⁽²⁾

SAE viscosity numbers	Viscosity range at 0° F (- 17.8° C)						Viscosity range at 210° F (98.9° C)			
	Minimum			Maximum			Minimum		Maximum	
	cP	cSt	SUS	cP	cSt	SUS	cSt	SUS	cSt	SUS
5W	1,200	1,300	6,000
10W	1,200 ^(a)	1,300	6,000	2,400	2,600	12,000
20W	2,400 ^(b)	2,600	12,000	9,600	10,500	48,000
20	5.7	45	9.6	58
30	9.6	58	12.9	70
40	12.9	70	16.8	85
50	16.8	85	22.7	110

(a) Minimum viscosity at 0° F may be waived provided viscosity at 210° F is not below 4.2 cSt (40 SUS).

(b) Minimum viscosity at 0° F may be waived provided viscosity at 210° F is not below 5.7 cSt (45 SUS).

(c) The viscosity of all oils included in this classification shall not be less than 3.9 cSt at 210° F (39 SUS).

(d) The official values in this classification are based upon directly determined viscosities at 0° F in centipoises and viscosities at 210° F in centistokes.

(1) Ref. (3).

(2) Abbreviations cP: centipoises; cSt: centistokes; SUS: Saybolt units.

and a variety of others. Only crankcase lubricants were included in this study.

An important characteristic of lube oils is the large amounts and variety of additives they contain. Among the most important are(2, 3):

- Viscosity index (VI) improvers. These are normally oil soluble polyolefins in the molecular weight range of 2,000-50,000 although methacrylate-fatty alcohol/ester copolymers and vinyl acetate/fumarate fatty alcohol copolymers are also used. These are often added in up to a few percent.

- Pour point depressants. These are usually aromatic-paraffin wax condensation products and alkyl methacrylate polymers. Vinyl esters and alkylated polystyrenes are also used. Pour depressors are present in less than one percent.

- Detergents and surfactants. Additives of this type are included to prevent sludge formation and to keep solid material in the lubricants suspended. These types of additives are usually metallic salts of sulfonic acid phenols, naphthenic acids and the like. The metals are normally of the alkaline earth type. They possess some water solubility and may be lost during weathering over salt water. Other dispersant additives, of a different nature are polyimides with branched (polyisobutene) side chains and certain methacrylate type copolymers. Detergent-dispersant additives may be present in from 0.1 to nearly 20 weight percent.

● Antioxidants. Oxidation of lubricants gives rise to harmful sludge or "varnish" deposits. Additives to prevent oxidation are usually oil soluble amines, phenols and sulfur or phosphorus containing organic molecules. In addition certain zinc salts of dialkyldithiophosphonic acids are common. The presence of large amounts of zinc is a good indication of a lubricant. Antioxidants are added in from 0.1-4.0 weight percent.

Additives may amount to as much as 20% of lubricant formulation(2). Since different manufacturers use different additives and since premium lubes have more and a greater variety of additives, these materials, if they can be identified, can be used to fingerprint a lube oil. How this can be done using IR and TLC is described in Section IV below.

I.1.5 Industrial White Oils

These are materials that are highly purified, colorless oils of high boiling ranges containing no aromatics. They are easily classified on the basis of these characteristics. Identification within the category, however, requires careful comparison with an authentic sample.

I.1.6 Marine Fuels

This group makes up a logical category for a separate discussion although we have classified them as to type (i.e., bunker, distillate, diesel, etc.), when including them in our analytical scheme. Marine fuels are of several broad classes:

- Bunkers
- Blended heavy fuels
- Marine gas oils
- Marine distillates
- Marine diesels
- Gasoline

I.1.6.1 Bunkers and Blended Resids

The use of bunker fuels in marine engines is fading. However, some ships will continue to use these heavy fuels for some time. Bunkers were described in Section I.2. Navy Special, a type of blended residual fuel was once the most common naval fuel. Specifications are given in Table 12. Navy Special fuel is designed for combat vessels while Naval "heavy" fuel is for non-combat vessels(8). The Navy Special fuel has characteristics somewhere in between commercial No. 4 and No. 5 oil (compare Tables 4 and 12) while the "heavy" grade is close to a No. 6 oil. These fuels would be readily classified as blended residual fuels but the Navy Special we examined had characteristics quite different from other blended resids and could easily be distinguished with the help of an authentic sample.

Table 12

Chemical and Physical Requirements
of Burner Fuel Oils (Military)*

	<u>Limits, Grade</u>	
	<u>Special</u>	<u>Heavy</u>
Flash point, closed cup (min.) °F	150	150
Fire point (min.), °F	200	200
Viscosity @ 122°F (max.), SSF		150
Viscosity @ 122°F (max.), SSU	225	--
Viscosity @ 85°F (min.)	225	--
Ash (max.), percent	0.10	0.12
Water, by distillation (max.) percent	0.5	0.5
API gravity (min.)	11.5	10.0
Pour point, upper (max.) °F	15	50
Carbon residue (max.), percent	15	--
Sediment by extraction (max.), percent	0.12	0.15
Water and sediment (max.), percent	0.5	--
Thermal stability (NBTL heater)	Pass	Pass
Explosiveness (max.), percent	50	50
Sulfur (max.)	3.50	--

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* From Ref. (8).

I.1.6.2 Marine Distillate Fuels

In this project we studied three types:

- Marine gas oil
- Marine diesel fuel
- Navy distillate fuel

In addition, marine gasoline (used by small boats and pleasure craft) and Navy Diesel fuel (the Navy "fuel of the future") need to be considered. Marine gasolines are similar to automotive gasolines (Section I.3) and need no special discussion here. Specifications for Navy Diesel Fuel are shown in Table 13. These requirements would make this diesel slightly heavier than a Class 3 diese (Table 7). Commercial marine diesels are very similar to Navy fuel although some are heavier [Class 4; final BP 800°F). Marine gas oils, however, are similar to Class 2 (automotive) diesels. They are designed for small deck engines and have a boiling range of 350-670°F(6).

Table 13

Chemical and Physical Requirements
of Navy Diesel Fuel*

Characteristics	Requirements	FED-STD-791 Test Method	ASTM Test Method
Ignition quality, cetane number (min.)	45-47		D 613
Water and sediment, percent, max.	0.01		D 2709
Distillation:			
50 percent point, °F	Record		
90 percent point, °F (max.)	675		D 86
End point, °F (max.)	725		
Flash point, °F (min.)	140		D 93
Pour Point, °F (max.)	0		D 97
Cloud point, °F (max.)	10		D 2500
Viscosity @ 100°F:			
Kinematic, centistokes	2.1-6.0		D 445
Carbon residue, on 10 percent bottoms, percent (max.)	0.20		D 524
Sulfur, percent (max.)	1.00		D 129
Corrosion (max.) (@ 212°F)	No. 1 ASTM		D 130
Color (max.)	5		D 1500
Ash, percent (max.)	0.005		D 482
Gravity (hydrometer)	Record		D 287
Demulsification, minutes (max.)	10	3201	--
Acid number (max.)	0.50		D 974
Neutrality	Neutral	5101	--
Aniline point, °F	Record		D 611
Accelerated stability, total insolubles mg/100 ml (max.)	2.5		D 2274

* Ref. (8) and MIL-F-16884F.

Navy Distillate Fuel was designed to be the replacement for Navy Special but it has now, in turn, been superseded by the Navy Diesel Marine fuel. However, many ships may be using the Navy Distillate fuel for some time. Specifications are given in Table 14. Comparison with Table 12 indicates the major differences between Naval Diesel and Distillate fuels specifications lie in the higher cetane number of the former and somewhat lower distillation range of the latter. The distillate fuel, in fact, is quite similar to a No. 2 domestic heating oil. The same general characteristics would be used to classify these fuels as other distillates (Section I.1.3).

Table 14

Specifications for Navy Distillate Fuel*

Gravity, API	27 Min.
Ash, %	0.01 Max.
Carbon Residue, 10% Bottoms, %	0.4 Max.
Cetane Number	39 Min.
Corrosion, Cu Strip 212°F, 3 Hrs.	2 Max.
Dist: 10% Evap. °F	500 Max.
50% Evap. °F	600 Max.
90% Evap. °F	660 Max.
95% Evap. °F	690 Max.
Emulsion Characteristics, Minutes	20 Max.
Explosiveness, %	50 Max.
Flash Point, °F	150 Min.
Neutrality	Neutral
Pour Point, °F	+25 Max.
Residuum Contamination	Pass
Sulfur, %	1.30 Max.
Vanadium, PPM	0.5 Max.
Viscosity, Centistokes @ 100°F	10 Max.
Water and Sediment by Centrifuge, %	0.020 Max.

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* MIL-F-24897.

The foregoing discussion was designed to point out the major characteristics one looks for in classifying oils. It must be emphasized again that these characteristics are general and cannot often be used for identification. They are no substitute for an artificially weathered, authentic sample.

I.2 Possible Fingerprinting Techniques

A variety of fingerprinting methods have been proposed. Except for those based on "active tags" these have mainly involved:

- Nickel/vanadium ratios
- Sulfur/nitrogen ratios
- Sulfur isotope ratios
- Internal reflectance spectrometry
- Ultraviolet absorption spectrophotometry (UV)
- Mass spectrometry (MS)
- Gel permeation chromatography
- Fluorescence spectrometry
- Paper and thin-layer chromatography (TLC)
- Infrared spectroscopy (IR)
- Gas chromatography (GC)
- Liquid chromatography (LC)

Several workers have employed various types of trace metal analysis for fingerprinting spilled oil(9-12). These methods have mostly involved nickel, vanadium, sulfur, nitrogen or ratios of these elements. Analytical techniques such as chemical/colorimetric, atomic absorption, x-ray fluorescence, emission spectroscopy and neutron activation analysis have all been employed and all have drawbacks(9). We have found measuring the Ni/V, S/N and S^{34}/S^{32} ratios to be too cumbersome, especially for weathered samples, for consideration as part of a simple, portable identification system. Internal reflectance spectrometry is claimed to have some advantages over infrared spectrometry(13). However, these seem to be more than offset by the greater simplicity of the latter method. Recently, Levy reported the use of ultraviolet method for characterizing heavy fuel oils and lubricating oils(14). He recommended the use of ratios of absorbances at 228 and 256 μ claiming these to be characteristic and not affected by weathering. However, only a very few examples are given and the spectra themselves are very similar. High resolution mass spectrometry is precise and highly discriminatory. It may well be the method of choice for a shore-based identification system. Such techniques are much too costly and complex for shipboard use. Gel permeation chromatography has been used to fingerprint oil samples(9,15), apparently with some success. We are recommending use of the closely related liquid chromatography as a useful fingerprinting tool.

We considered all of the above techniques before deciding on TLC, IR and GC, along with certain physical measurements to serve as a basis for developing our system. Later, with the approval of the contract monitors,

LC was added in place of physical measurements and some of the GC determinations. This is discussed in Section IV below. A short introduction into previous work in the areas of choice is appropriate here.

I.2.1 Use of Thin-Layer Chromatography

Little has been done to develop this method although Herd(16) has recommended using paper chromatography to identify oils. We have found TLC superior to paper chromatography for nearly all applications.

Certain specific types of hydrocarbons have been separated as described by Stahl(17) and Crump(18). The latter chromatographed various types of oils including, some hydrocarbons, on silica gel using benzene-chloroform as the eluting solvent. Stahl recommends an activated absorbant and an "only slightly polar solvent." He points out that saturated hydrocarbons migrate faster than olefins or aromatics on inorganic absorbants(17). Matthews(19) used various absorbants and solvents to separate different "classes" of petroleum and coal tar residues. His method, however, is somewhat complex and requires several separate tests.

Advantages of TLC include speed, ease of operation and interpretation and the fact that only traces of material are required. The major disadvantage lies in the low resolving power of the system and the fact that many oils behave quite similarly.

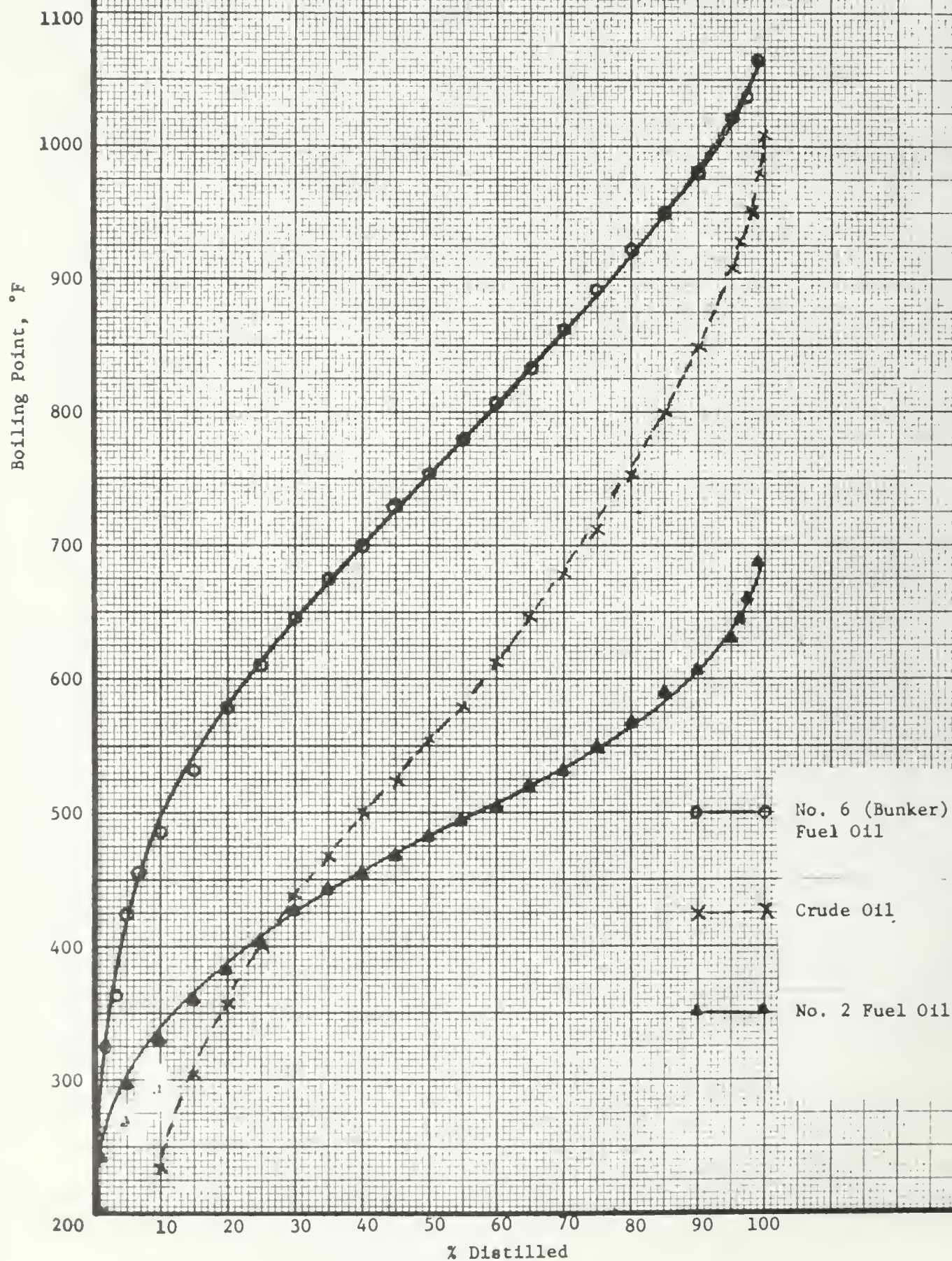
I.2.2 GC Distillation (GCD)

An accurate picture of the volatility profile for a given petroleum product is afforded by this technique. Precise data of boiling point vs. percent distilled are obtained on very small samples. Some typical curves obtained by plotting percent distilled vs. boiling point for some different types of petroleum products are shown in Figure 1. The shapes of these curves are characteristic and are quite different for crudes and refined products. Our work on the chemistry of weathering (1) indicates this characteristic shape does not change appreciably on moderate weathering but is simply displaced to higher average boiling points. As a result, much may be learned of the type of petroleum product by the shape of this curve alone. Even some crudes, which might be expected to have similar curves, may be distinguished by this method. The GCD trace may also be used to fingerprint oils. Examples are given in Section IV. Recently, Bentz and Hoberecht (20) described how this method can be applied to oil spill identification.

GC distillation data may also be used in conjunction with specific gravity as described in the following subsection.

Figure 1

GC Distillation Curves for
Different Types of Petroleum Products



I.2.3 Average Boiling Point/ Specific Gravity Ratios

Plots of specific gravity vs. percent boiling below 500°F for various petroleum products studied in our weathering program are shown in Figure 2 (1). These plots are quite linear, at least for moderate (up to two weeks) weathering periods. Of especial interest is the fact that all crudes we have studied so far show well separated parallel lines. Thus, a number of oils may be eliminated as possible sources of a spill by plotting the appropriate values for a sample, even if the weathering time is unknown, provided standard curves are available. Our tests have shown that weathering conditions do not greatly affect the characteristic slopes. This is illustrated in Figure 3 where values for "real marine" samples are compared with laboratory standard curves. These samples were obtained at three outdoor weathering locations as described in Ref. (1). Neither weathering conditions nor times were accurately known. The agreement is quite good. As might be expected, refined products such as fuel oils show different slopes from crudes. Hence, some points for a fuel oil might fall on one of the curves for a crude. The shape of the GCD curve or one of the other methods would resolve this ambiguity with no difficulty.

I.2.4 Infrared Fingerprinting

Infrared spectrometers are readily available and portable. Our experience has shown they are useful tools for oil identification as well. Most petroleum products have characteristic fingerprints and many can be distinguished at a glance. Spectra from very similar oils, however, may require some experience in interpretation. To avoid this, the method suggested by Kawahara(21) may be used. He compared ratios of transmittance at various frequencies for a number of oils and found sufficient differences to characterize the oils he investigated. Some recommended ratios are $720\text{ cm}^{-1}/1375\text{ cm}^{-1}$; $3050\text{ cm}^{-1}/2925\text{ cm}^{-1}$; $1600\text{ cm}^{-1}/720\text{ cm}^{-1}$ and $1600\text{ cm}^{-1}/1375\text{ cm}^{-1}$. This has been criticized by Mattson et al(13) who feel that qualitative examination of the entire spectrum is preferable to looking at only certain ranges(9,13).

The use of IR as a fingerprinting tool has several attractive features:

- In the hands of an experienced person it provides perhaps the most definitive identification of an unknown material with an authentic sample.
- It is a simple and rapid technique and spectra can be run in dilute solution or on neat smears; only trace quantities are required.
- It is non-destructive and the sample can be recovered.
- Instrumentation is readily available.

Figure 2
Plot of Specific Gravity
vs. % Boiling <500°F

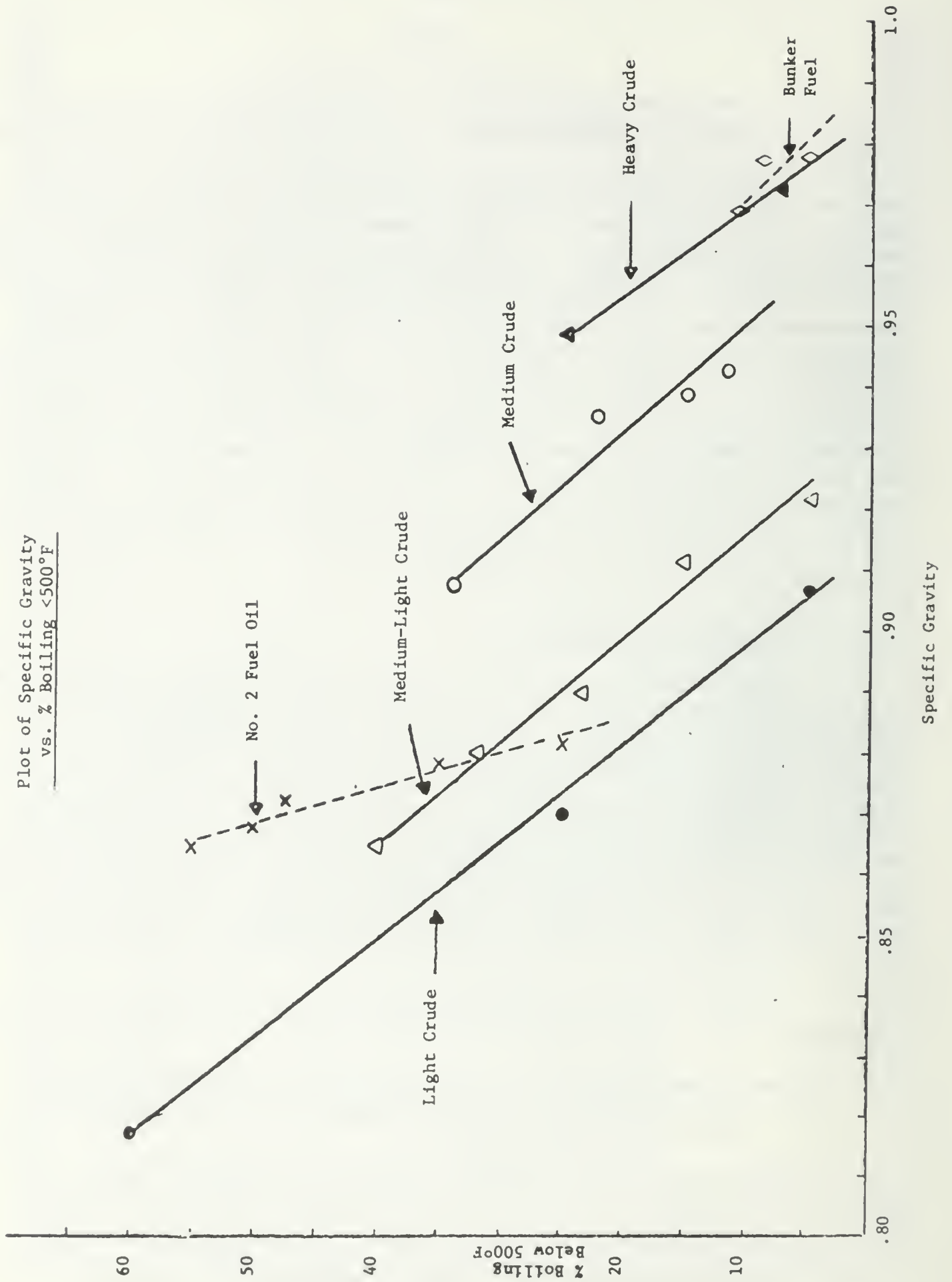
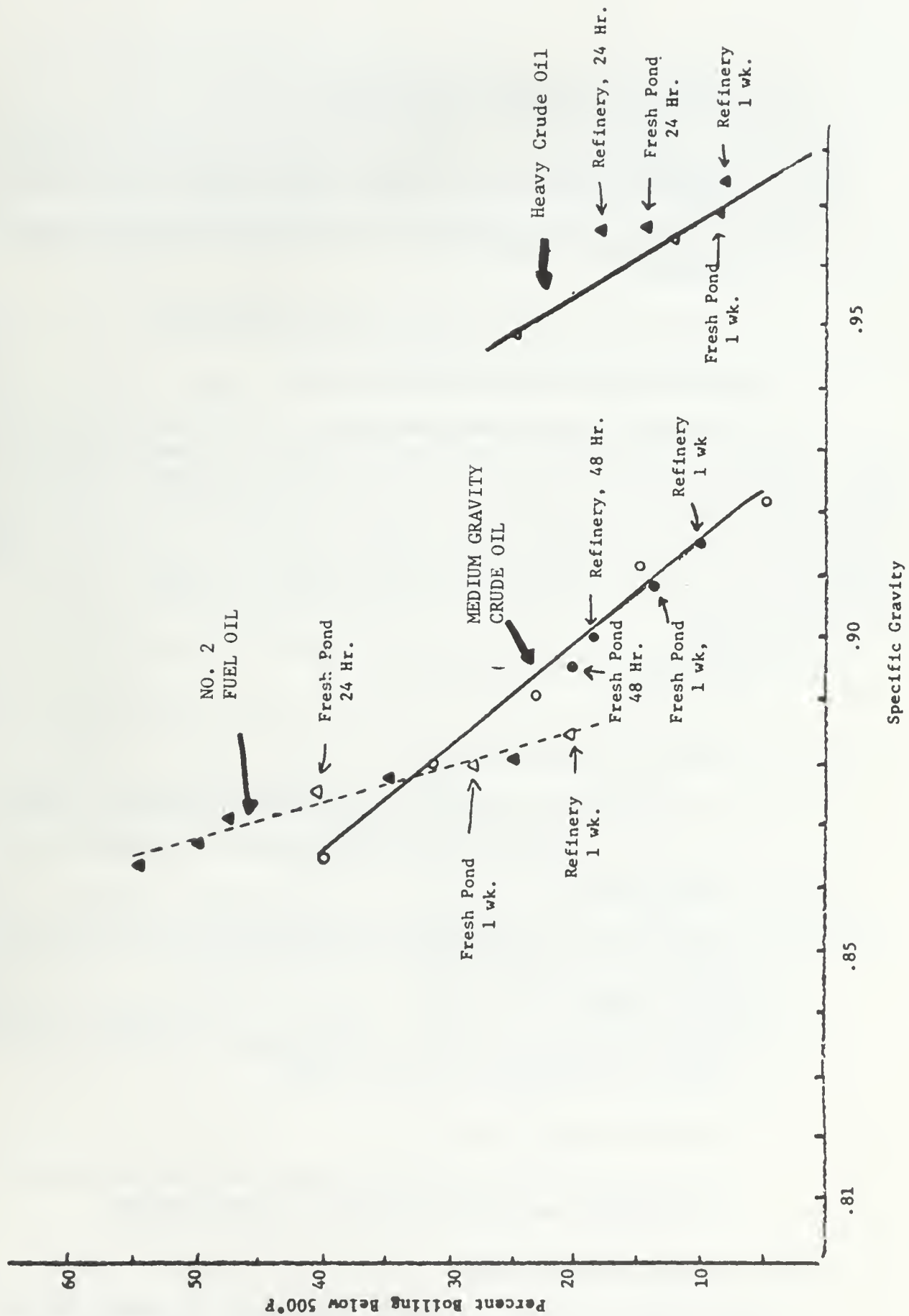


Figure 3

Plots of Specific Gravity vs. Distillation Data
For Real Marine Samples - Comparison to Laboratory Standard Curves



But also has potential drawbacks:

- Some experience is needed in comparing spectra, especially since the effects of weathering are unknown and variable.
- It has limited usefulness as a general classification method.
- Impurities in sample may cause difficulties.

I.2.5 Gas Chromatographic Fingerprinting

Petroleum products have characteristic GC traces. Frequently, these differ so greatly that even poorly resolved chromatograms such as those obtained in GC distillation are sufficient for identification. The GCD chromatograms are run on a 2-ft. W-98 column. Certain crudes, especially the aromatic ones, and some heavy fuels may require more highly resolved chromatograms to distinguish them. These may be obtained on the same instrument as for the GC distillations by going to longer columns. We use 15' SE-30 columns.

This method is advantageous in:

- Having good resolving power for crudes and light to medium refined products.
- Being simple to operate and requiring very small samples.
- The fact it can be made quantitative by comparing certain peak ratios.
- Instruments are available and techniques well worked out.

Disadvantages:

- Poor resolving power for certain heavy refined products such as lubricants and white oils.
- Impurities may interfere.
- Pretreatment of crudes and heavy fuels may be necessary to prevent rapid deterioration of the columns.

I.2.6 Liquid Chromatography

This method has only recently been used for identification purposes(24) and techniques are still not perfected. However, we have been developing this technique for use in analyzing certain petroleum products and feel it should be useful in fingerprinting.

This method makes use of a high pressure liquid chromatograph equipped with columns of small-particle silica packing operating in the absorption mode. Elution is normally with a non-polar solvent such as iso-octane but others can be used. Several detectors are possible. We have used, simultaneously, an ultraviolet (UV) detector in series with a refractive index (RI) sensor. This affords two traces for each sample through. The UV detector senses largely aromatic compounds while the RI detector records the total sample. Thus two, very different fingerprints are obtained.

This method shows promise in being:

- Relatively rapid
- Versatile - different packing solvents and detectors can be used
- Simple to evaluate

and in the fact that:

- Two traces are obtained for each sample.
- Impurities, especially polar materials, will not interfere.

Some drawbacks:

- Sample injection requires some practice.
- Weathered samples are more difficult to evaluate. Artificially weathered authentic samples may be necessary even for accurate classification.

The foregoing subsections are designed to introduce the various analytical methods and the rationale for their choice. It must be emphasized that, although several of the methods can classify materials broadly without an authentic sample, it appears that no single method will suffice for identification. Nor is identification likely with a high degree of accuracy in the absence of an authentic sample, preferably artificially weathered.

II. OBJECTIVES AND TASKS

The major objectives of this project were:

- (1) To test the fingerprinting methods described in the previous section on a wide variety of petroleum products to determine their ability to identify the class or category of the oil.
- (2) To determine the potential of these methods for distinguishing among oils of the same class.
- (3) To decide which of the candidate methods are useful and integrate them into an identification **system**.

In order to test as many different petroleum samples as possible with available funds it was not an objective of this work to investigate, in detail, sample handling techniques. Nor were we constrained to work with trace quantities or oil films. However, we were cognizant of the need to be aware that the final method or methods must be capable of being adapted to such samples. In addition, the characteristics of an "ideal" fingerprinting scheme, as described in Section I, were constantly borne in mind and served as an aid in the final choice of the best methods.

In order to meet these objectives, the following tasks were designed:

- (1) Selection and Procurement of Test Oils
- (2) Weathering Experiments
- (3) Preparation of Samples
- (4) Analysis of Samples
- (5) System Selection and Refinement
- (6) Recommendations and Reports of Work

III. EXPERIMENTAL SECTION

The experimental part of this program consisted of carrying out the tasks outline in the previous section.

III.1 Task (1) - Selection and Procurement of Test Oils

A total of 57 oils was obtained. These were selected from the following classes of petroleum products.

- Crude Oils. Fifteen different ones were obtained from all over the globe exhibiting a wide variety of physical and chemical properties.

- Residual Fuels. One Bunker "C" was obtained.*

- Blended Residual Fuels. Fourteen were obtained from various sources. They are broken down by types as:

- + No. 4 Fuel Oils (three samples)
- + No. 5 Fuel Oils (four samples)
- + No. 6 Fuel Oils (six samples)
- + Navy Special Fuel (one sample)

- Distillate Fuels. Sixteen representing the following types:

- + No. 2 Heating Oils (eight samples)
- + Diesel Fuels (four samples)
- + Jet Fuels (two samples)
- + Gasolines (one sample)
- + Navy Distillate Fuel (one sample)

- Lubricating Oils. Various grades (ten samples).

- Miscellaneous Petroleum Products. (three samples).

- + White Oils (two samples)
- + Outboard Motor Oil (one sample)

The test oils were procured from several commercial sources. In accordance with contract stipulations they were given code numbers and all reference to them in this report will be by code number and class of oil only. No commercial sources will be revealed. The code system used is as follows:

* Although obtained as a straight-run residual fuel, this sample turned out to be a blended resid (see Section IV.3.2).

Explanation of Coding System
for Test Samples

Sample No.:	10	-	A	-	1	-	I
	Oil		Company		Individual		Weathering
	Category		Code		Sample		History
					No.		

Category Code

- 10 = Crude Oils
- 20 = Residual Fuels (Bunker C)
- 30 = Blended Residual Fuels
 - 30 = No. 4 Fuel Oil
 - 31 = No. 5 Fuel Oil
 - 32 = No. 6 Fuel Oil
 - 33 = Navy Special Fuel
- 40 = Distillate Fuels
 - 40 = No. 2 Heating Oil
 - 41 = Kerosene and Gas Oil
 - 42 = Diesel
 - 43 = Jet Fuel
 - 44 = Gasoline
 - 45 = Navy Distillate Fuel
- 50 = Lubricating Oils
- 60 = Miscellaneous

Weathering History Code

- 0 = Unweathered
- I = Weathered 1 day
- II = Weathered 1 week
- III = Weathered 2 weeks

A complete listing of coded oils obtained is included in Appendix A to this report.

III.2 Task (2) - Weathering Experiments

Two different techniques were investigated: (1) two week runs in laboratory simulators, and (2) rapid artificial weathering of "authentic samples."

III.2.1 Two-Week Laboratory Weathering Experiments

The apparatus employed* is pictured in Figure 4 and diagrammed schematically in Figure 5.

The main function of this facility was to provide a means of simulating and controlling the environmental (weathering) variables being tested as well as other important environmental conditions which were fixed during the experiments. The main components of this facility included:

- A continuous water recirculation system.
- A reservoir (stainless steel drum) for holding the salt water.
- A Teflon coated, baffled tank to hold the oil samples.
- A cooling coil refrigeration system to chill the salt water.
- A Teflon coated magnetic stirrer.
- An ultraviolet lamp to simulate exposure to the sun.
- A fan to simulate wind currents.

Ten separate individual rigs of the type described in Figures 4 and 5 were used in this program. Each operated independently (except for the water chiller cooling coils which were connected in parallel to a water chiller).

In operation, ocean water was continuously pumped from the stainless steel drum into the Teflon coated tank by a Teflon magnetic pump. In the Teflon coated tank, the water continuously "washed" the test oil sample and then was returned to the drum by gravity. An under flow baffle in the Teflon coated tank allowed the passage of water but prevented the oil sample (which remained on the water surface) from leaving the tank. A Teflon coated bar, activated by a magnetic stirrer, provided additional mixing in the tank.

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* Ten of these simulators were constructed under a contract with the Environmental Protection Agency who generously permitted them to be used on this project.

Figure 4
Laboratory Weathering Simulator

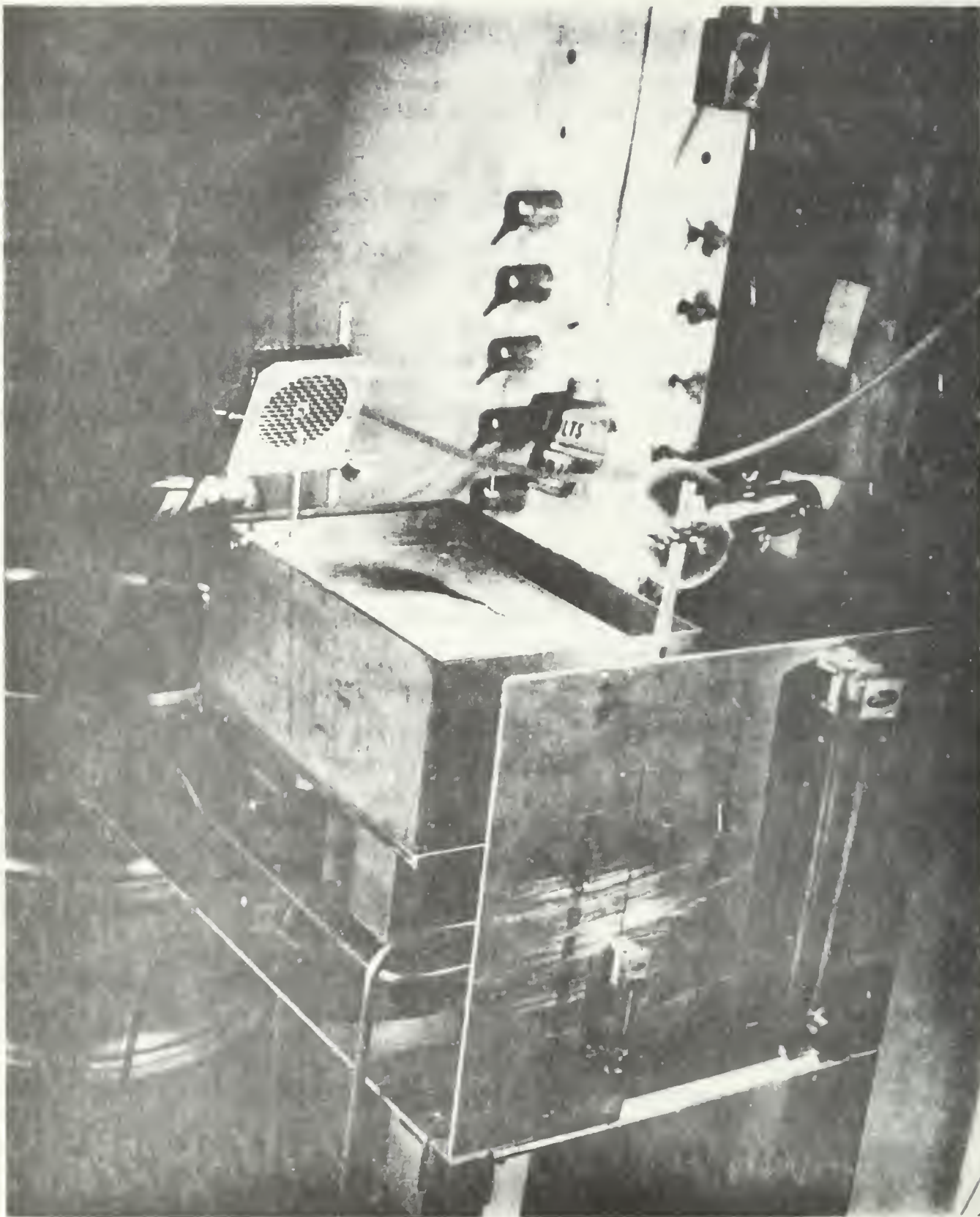
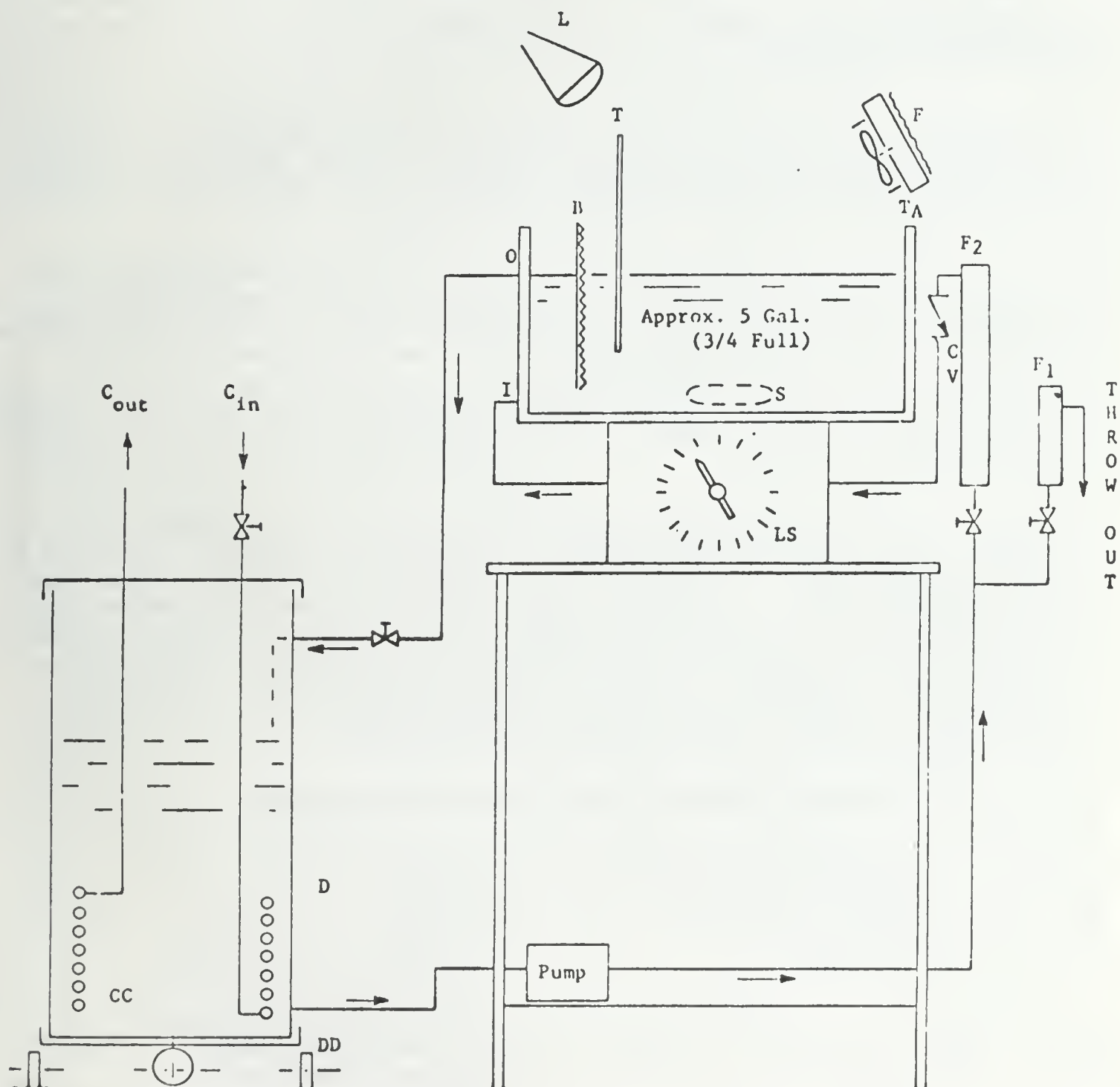


Figure 5

Schematic Diagram of Weathering Simulator



B - Teflon coated baffle
 C_{in}, C_{out} - Chilled water in and out
 CC - Cooling coil (S.S.)
 CV - Check valve
 D - S.S. drum (55 gal.)
 DD - Drum dolly

F - Fan, F₁ - 5 to 50 cc/min, F₂ - .3 to 60 GPM
 I - Tangential inlet
 L - Programmed on-off sunlamp
 LS - Rotating magnetic stirrer
 O - Overflow
 T - Thermometer stirring magnet
 T_A - Teflon coated tank
 S - Stirring Bar

A G.E. model 78 ultraviolet lamp was used to provide simulated sunlight to the oil samples. Mounted to shine directly on the surface of each tank, the ultraviolet lamps were connected to a special electric timer circuit that provided two hours a day of lamp on time. At the selected distance of each lamp from the oil surface, this exposure time provided an ultraviolet dosage comparable to a cloudless full summer day in the mid-northern hemisphere.

A constant speed fan, mounted on each tank, simulated exposure to constant wind of about 15 mph. The salt water used in these tests was obtained from the New Jersey shore, Manasquan Inlet, on the incoming tide. This water was surprisingly clean, containing only .02-.04 ppm of dissolved organic material, and had low bacterial count(1).

The weathering tests were conducted by establishing steady state conditions of water temperature, recirculation rate and magnetic stirrer speed and then adding a fixed quantity of the test oils to the salt water in the Teflon coated weathering tanks. The amount of oil used was 100 cc. This afforded a slick thickness of about 0.1 cm at the beginning of the experiment, somewhat thicker than that observed in field tests(25). However, this was the minimum quantity of oil which would provide sufficient samples for testing.

Salinity measurements were taken periodically by means of a hydrometer. The values were compared to a standard curve (Figure 6) obtained by plotting hydrometer readings vs. water temperature for the sea water used in the experiments. The plot is quite linear over the rather narrow range of temperatures used in these studies. If the salinities in the simulators differed significantly from the standard value for the given temperature adjustments could have been made by adding distilled water or "synthetic sea salts."* Temperature was also carefully monitored. The following weathering conditions were maintained as "standard."

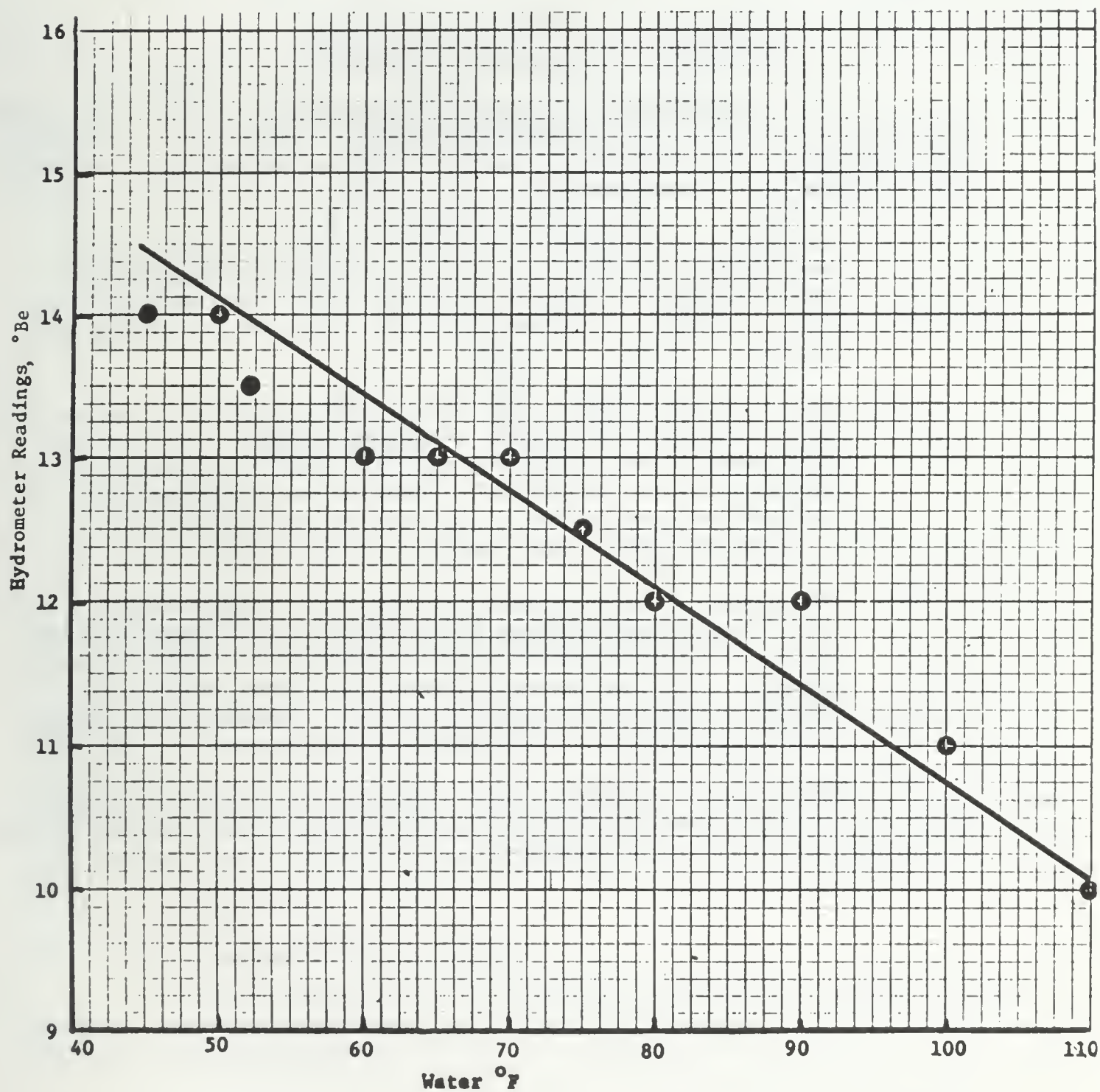
Standard Conditions for Weathering Experiments

Slick Thickness:	0.1 cm
Air and Water Temperature:	Ambient (72- 80°F)
Total Water Wash:	50 gal.
Wash Rate:	3 gal/min.
UV Light:	4 hr/day (roughly equivalent to 8-10 hrs. of sunlight on cloudless day in northern hemisphere).
Fan:	Constant (approximates 15 mph wind)
Water:	Ocean

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* Obtained from Lake Products, Inc., St. Louis, Missouri. In actual practice no salinity adjustments were necessary during the two-week weathering periods employed in this study.

Figure 6

Temperature vs. Salinity Plot for Manasquan Sea Water



A log of ambient conditions for the various sets of experiments is given in Appendix C. Additional details of this procedure can be found in Ref. (1) which also discusses the close relationship between laboratory and "real marine" weathering results.

III.2.2 Accelerated, Artificial Weathering Experiments of "Authentic Samples"

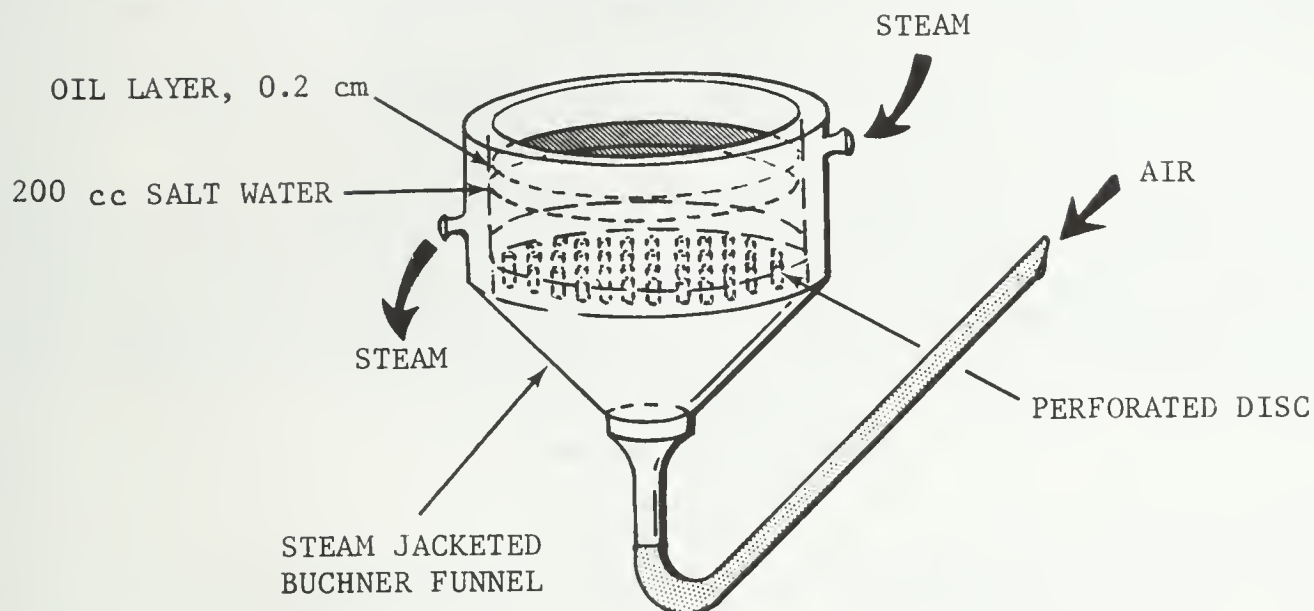
These experiments were aimed at developing a simple, rapid technique for artificially weathering an "authentic" sample of a suspected pollution source to facilitate comparison with an actual spill material. Three methods were investigated.

- (1) Small 1-2 cc portions of a crude oil (10-A-1) and a No. 2 heating oil (40-A-1) were placed in crystallizing dishes and heated in a vacuum at 70°C and about 1 mm pressure for 3 hr. and 20 hr. The residues were analyzed by GC and LC methods.
- (2) Approximately 20 cc of oil was floated on 500 cc of water containing 15 g of NaCl in a stirred beaker. The mixture was heated to 80°C over a steam bath while a stream of air was passed over the surface. Heating was continued for one and two hour periods. The oil phase was separated in a separatory funnel and analyzed by GC and LC.
- (3) The apparatus used is shown in Figure 7. Approximately 35 cc of oil (affording a 0.2 cm thick layer) was added to 200 cc of water containing 6 g of NaCl in the steam jacketed funnel. Steam was passed through the funnel and air was bubbled slowly up through the mixture. Samples were taken at 1 hr. and 4 hrs. and analyzed as in methods (1) and (2).

Results are discussed below (Section IV). Method (3) gave excellent results; the "weathered" oil closely resembled a two-week sample of the same oil from the simulators.

Figure 7

Accelerated Weathering Apparatus



III.3 Task (3) - Preparation of Samples for Analysis

The procedure for preparing test oils for analysis is outlined in Figure 8. Approximately 10 cc samples were removed from the simulators at 24 hrs., 1 week and 2 weeks. The samples were centrifuged for 10 minutes at about 6,000 rpm and then stored under nitrogen in brown, screw-cap bottles. Specific gravities and infrared (IR) scans were taken on the neat smears and then an equal volume of n-pentane was added and the samples thoroughly shaken. The pentane extracts were then used directly for gas chromatography (GC) and thin-layer chromatography (TLC).*

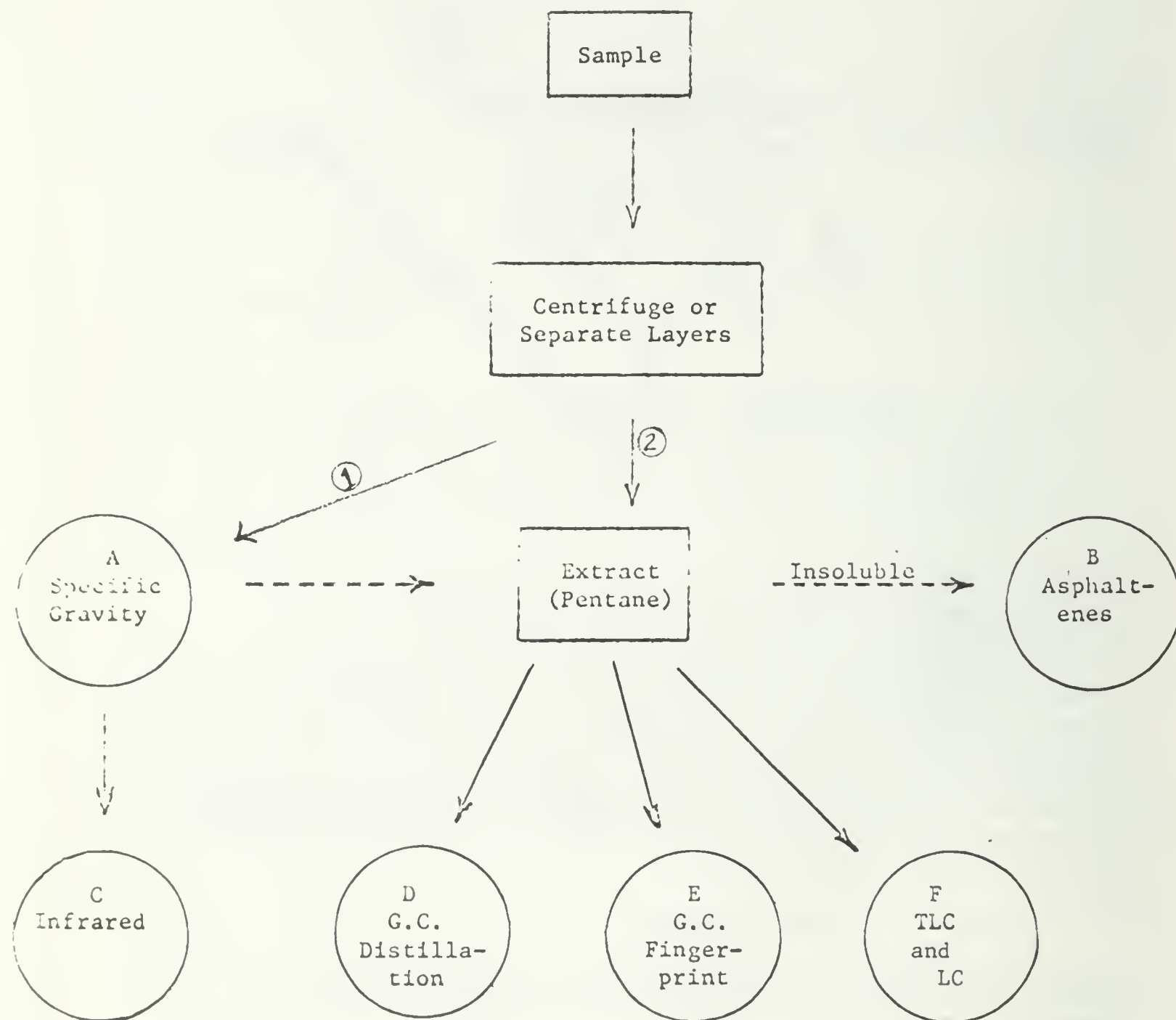
III.4 Task (4) - Analysis of Samples

A brief description of analytical methods will be given in this section. Additional details may be found in Reference (1) and in Appendix A to this report.

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* If sufficient sample was available (5 cc or more) it was divided in two, one portion used for IR and GC work and the second for specific gravity and TLC. This was to speed up analytical work and to minimize weathering during sample handling.

Figure 8
Sample Treatment Scheme



III.4.1 Specific Gravity Determinations

Two methods were used. The first of these is the standard technique employed by the oil industry. Precision of $\pm 0.1\%$ is achieved (Ref. (1) and Table 15) but a relatively large sample (2-5 cc) is required. As a result, a micromethod was developed which requires very small quantities but gives somewhat poorer precision (Table 16).

III.4.1.1 Specific Gravity Determinations by Standard Method

Weathered oil samples were centrifuged at 6000 rpm to remove suspended water. The specific gravity was determined using 2 or 5 ml specific gravity bottles of the Gay-Lussac type* and a Mettler Gram-matic balance (model B-5, H-26)** weighing them by difference. The results were calculated and corrected to standard conditions as shown on a sample form in Figure 9. With practice, precision of better than $\pm 1\%$ can be achieved (Table 15).

Table 15

Precision of Specific Gravity Measurements

Oil	Weathering Time(1)	Specific Gravity of Replicates				
		A	B	C	D	Ave.
No. 2 Fuel Oil	0	0.8641	0.8634	0.8633	0.8632	0.8636
No. 2 Fuel Oil	48 Hr.	0.8808	0.8813	0.8796	--	0.8806
Heavy Crude	1 Wk.	0.9724	0.9731	--	--	0.9728
Light Crude	0	0.8168	0.8178	0.8163	--	0.8174
No. 2 Fuel Oil	24 Hr.(2)	0.8735(3)	0.8743(3)	0.8746(3)	--	0.8742

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(1) At 80°F unless otherwise specified.

(2) At 55°F.

(3) Represents separate weathering experiments, not replicates.

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* Lab Glass Inc., Vineland, New Jersey.

** Fisher Scientific Co., New York, New York.

Figure 9

DENSITY AND SPECIFIC GRAVITY OF LIQUIDS BY PYCNOMETER

Observed Temperature 77 °F (25 °C)

Date: 10-2-73

Oil Sample: 10-A-2-I

SAMPLE IDENTIFICATION	WATER	10-A-2-I		
A. Total weight, g	14.0687	13.3926		
B. Empty Pycnometer, g	8.9984	8.9983		
C. Net weight g. (A - B)	5.0703	4.3943		
D. Specific gravity at observed temp. °F/°F (C _{sample} ÷ C _{water})		0.8667		
E. Density of water at <u>77</u> °F "Handbook (See Tables) of Chemistry"	0.99704			
F. Volume of pycnometer at observed temp, inl (C ÷ E)	5.0853			
G. Density of sample at observed temp. ____ °F (C ÷ F)		0.8641		
*H. Density of sample at 60°F, g/cm ³		0.8700		
I. Specific Gravity of sample at 60°/60°F (H ÷ .99905) ^d		.8708		

*H. Density of sample at 60°F = Density at observed temp. (1 + Δtβ) = 0.8641 (1.0068)

where Δt = observed temp, °F - 60°F = 15.2

β = coef. of expansion of oil sample

See Tables for proper value (ASTM Table 7) = .0004

^d .99905 = wt. of 1 cm³ of water at 60°F relative to 1 at 4°C.

III.4.1.2 A Microanalysis for Specific Gravity Measurements

In order to obviate the need for large samples we have investigated an alternate procedure using disposable micropipettes instead of specific gravity bottles. These pipettes are readily available and are calibrated quite accurately. Only 50-100 ul of oil are required. Otherwise the procedure is the same as when using specific gravity bottles. Some results are given and contrasted with the more conventional methods in Table 16. Agreement is fair and, with practice, could be improved.

Table 16

Comparison of Micro and Conventional Determinations of Specific Gravity

<u>Oil(2)</u>	<u>Specific Gravity by Micropipette(1)</u>				<u>Conventional Method(3)</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>Ave.</u>	
Crude, 10-A-1	0.946				0.9501
Crude, 10-A-2	0.797	0.800	0.798	0.798	0.8187
Crude, 10B-1	0.836	0.838		0.837	0.8194
No. 2 Oil 40-A-1	0.856	0.873		0.864	0.8678

- - - - -

- (1) Numbers refer to duplicate determinations; these values are not converted to standard conditions.
- (2) Unweathered samples only.
- (3) Specific gravity bottles, requires 2-5 ml samples.

III.4.1.3 GC Distillations

The chromatographs were run on a 1/4" x 2' W-98 on Chromasorb G column in a Hewlett Packard #7620 dual column gas chromatograph fitted with an Infotronic CRS-100 integrator modified for 30 second printout. The instrument was programmed from 50-375°C at a rate of 10°/min. If the samples were quite fluid they were injected neat. Heavily weathered, highly viscous samples were dissolved in xylene or n-pentane before injection. Sample size was about 3 µl.

Standard curves of retention time vs. boiling point were obtained before each series of runs using mixtures of pure hydrocarbons. Comparison of integrator printout to the standard curve afforded a series of boiling points for a given percent distilled. Typical plots of boiling points vs. percent distilled as well as the chromatograms themselves may be found in Section IV.

III.4.1.4 GC Fingerprinting

More highly resolved chromatograms than those from GC distillations were obtained using a 15', 1/8" stainless steel column packed with 3% SE-30 on 80/100 Supelcoport. The instrument was a Perkin Elmer model 900 gas chromatograph operating under the following typical conditions:

Gas flow rate:	30/30 cc/min.
Temperatures:	Block, 330°C, Inj. 330°C Start 60°C, Hold, 350°C Program, 8°/min.
Detector:	Flame
Sample size:	0.5 ul (neat)
Attenuation:	R 100 x 128
Chart speed:	1/2 in./min.

III.4.1.5 Infrared Spectrometry

Infrared spectra were run either as neat smears between KBr plates with a 0.05 cm spacer or in 0.0538 cm, fixed path length, cells depending on the viscosity of the sample. A Beckman IR-12 was the instrument employed.

Some preliminary experiments, using samples generated in a previous project(1) were conducted to compare the ATR reflectance technique to direct radiation through a fixed path length KBr cell. The ATR spectra were obtained using a KRS-5 (Thallium-Br/I) crystal. From both the convenience and quality of spectra standpoints, the fixed path length technique seems superior. It was found that for very fluid samples (e.g., a No. 2 oil) smears were difficult to maintain on the KRS-5 crystal. In addition, such crystals are fragile, toxic and rather expensive. The better resolution obtained in the case of the fixed path length cell is illustrated in Figures 10 and 11. It is especially noticeable in the 600-900 cm^{-1} region of the spectra. As a result all spectra discussed in this report were obtained in the fixed path length cells.

III.4.1.6 Thin-Layer Chromatography

This was a feasibility study rather than a study to develop a method. As a result a variety of spotting methods, adsorbents, eluting solvents and visualizing techniques were investigated. The following procedure, which cannot yet be considered optimized, has given the best results.

Test solutions were made by dissolving five drops from an ordinary medicine dropper in 3 cc of high purity hexane. Approximately 5 microliters of the test solutions were spotted* about 1 cm from the bottom of a commercial glass plate coated with an 0.1 mm layer of cellulose F** or an 0.25 mm

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* Some samples were streaked horizontally along the plate. Spotting gave better results.

** Brinkmann Instruments, Inc., Westburg, New York.

IR Scan of Weathered No. 2 Oil Using Fixed Path Length KBr Cell



layer of silica gel 60F* and eluted with a variety of solvents for 15 cm in an ascending manner. A closed chamber was used but it was not solvent-saturated. Development time in unsaturated chambers was 1/2 - 1 hr. After air drying for a few minutes the plates were irradiated, first with long wave (3600Å) UV light, then with short wave light (2500Å). Spots or zones which appeared were marked with pencil and the plates were sprayed with con. H₂SO₄ or a H₂SO₄ - dichromate solution and charred in an oven at 120° for 1/2 to 1 hr. In other experiments the chromatograms were visualized by storing the developed plates in chambers saturated with iodine vapors for from 10 min. to 24 hr. Dark brown spots or zones were obtained.

III.4.1.7 Analysis by Liquid Chromatography

The liquid chromatograms were obtained on a Waters Associates Model 202-401 analytical liquid chromatograph with a 4' x 1/8" Porasil column operating at a pressure of 1000 psi. The flow rate was 1 ml./min. with isooctane as the solvent. A ultraviolet (UV) and a refractive index (RI) detector were used in series and afforded two different traces for each sample. The samples, in isooctane, were injected directly on-column through a septum.

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* SGA Scientific Inc., Bloomfield, New Jersey.

IV. RESULTS AND DISCUSSION

This section represents a continuation of Task (4), the analysis of samples and a part of Task (5), system selection and refinement. Emphasis will be placed on interpreting results in light of assessing the relative usefulness of each analytical method and in pointing out how the method may best be used as part of a classification-identification scheme. Each type of analysis will be discussed separately; integration into a system will be the subject of Section V and the Appendices.

The spectra included will be only those necessary for illustration. Reproductions of all spectra will be delivered to the U.S. Coast Guard R&D Laboratories, Groton, Connecticut.

A number of repeat weathering experiments and analyses were run to determine the reproducibility of the methods. This was generally quite good and will be discussed in a separate subsection (IV.9, below).

IV.1 General Weathering Observations

This subject was discussed in considerable detail in a prior report (1). However, a few additional comments are appropriate in areas that directly affected the current program.

The observations this time were in good agreement with those made previously (1) if one allows for minor changes due to differences in slick thickness and average air temperatures. Evaporation and dissolution were, again, the predominant weathering processes for the first few days. Loss of volatile components from the light products, gasoline and jet fuels was so rapid that insufficient material remained after 12 hrs. to obtain a sample. Some of the diesel fuels and light heating oils were also affected and some samples had to be omitted. Loss of certain water soluble additives was also noted in some refined products, notably lube oils.

Oxidation was an important aspect of weathering for many of the No. 2 heating oils and some crudes. This was evidenced by the appearance of a strong band at 1700 cm^{-1} ($\text{C}=\text{O}$) in the IR spectra of these materials. This band was apparent after one week and, in the case of heating oils, was very strong after two weeks. This phenomenon which we have attributed to olefin oxidation (1) is so prevalent in heating oils that it is almost characteristic. It is likely most prevalent in such oils which contain large amounts of catalytically cracked stock.

IV.2 Specific Gravities as a Fingerprinting Tool

These determinations were not made for all samples since it soon became apparent that this method was more tedious, required large sample sizes and gave less useful results than other types of analyses.

The specific gravity measurements were made in duplicate or triplicate whenever possible. Some selected results are shown in Table 17. Complete results, for the oils analyzed this way, are given in Appendix D.

Table 17

Specific Gravity Determination

Sample	Type of Oil	Weathering Time	Specific Gravities ^{(1), (2)}		
			Average	Range	Standard Deviation ⁽³⁾
10-A-3-0	Crude	0	.8659 ⁽⁵⁾	.8656-.8662	.0004
I		1 day	.9014 ⁽⁵⁾	.8999-.9029	.0015
II		1 week	.9109 ⁽⁵⁾	.9102-.9113	.0005
III		2 weeks	.9155	.9155-.9157	--
40-A-1-0	No. 2	0	.8678 ⁽⁴⁾	.8674-.8685	.0007
I		1 day	.8777	.8769-.8784	--
II		1 week	.8831	.8876-.8836	--
III		2 weeks	.8805	.8803-.8813	--
42-A-1-0	Diesel	0	.8446	.8446-.8446	--
I		1 day	.8474	.8470-.8477	--
II		1 week	(6)	--	--
III		2 weeks	(6)	--	--
10-A-2-0	Crude	0	.8182 ⁽⁵⁾	.8175-.8187	.0006
I		1 day	.8723	.8718-.8728	--
II		1 week	.8810 ⁽⁷⁾	--	--
III		2 weeks	.8843 ⁽⁷⁾	--	--
60-X-2-0	White	0	.8821	.8820-.8822	--
I	Oil	1 day	.8814	.8808-.8817	--
II		1 week	.8812 ⁽⁴⁾	.8804-.8821	.0010
III		2 weeks	.8814	.8810-.8817	--
50-A-1-0	Lube	0	.8856	.8851-.8861	--
I	Oil	1 day	.8829	.8828-.8830	--
II		1 week	.8836	.8832-.8841	--
III		2 weeks	.8844	.8841-.8846	--

(1) Average of two determinations unless otherwise noted.

(2) "0" designates unweathered sample.

(3) Obtained for triple and quadruple determinations only; calculated by multiplying range value x .5907 (3 detn.) or .4857 (4 detn.).

(4) Three determinations.

(5) Four determinations.

(6) Insufficient sample for this analysis.

(7) One determination only.

Specific gravities for weathered and unweathered bunker "C" (sample 20-A-1) could not be obtained by our present methods. A special, wide-mouth specific gravity bottle (1) is required which can be heated. These are readily available. Missing from Table 3 are 1-week and 2-week values for the automotive diesel, 42-A-1. This material weathered so rapidly that insufficient material remained after a week for specific gravity determination by present methods. Fortunately, enough sample was obtained for the other analytical techniques.

A plot of specific gravity vs weathering time is given in Figure 12. In general, these have the same shapes observed previously (1). Small changes may be ascribed to higher weathering temperatures, thinner films and fewer points to which to fit the curves. As expected, the more highly refined the material the flatter the curve. This continues all the way down to the white oil (60-X-2) which consists almost entirely of branched and normal paraffins. This material shows no change in specific gravity with weathering (Table 17, Figure 12). This is also true of the lube oil 50-A-1, a highly refined material whose compounds exhibit a very narrow range of physical properties.

The use of specific gravity as a fingerprinting tool is somewhat limited unless the weathering history of the samples or some other property (such as average boiling point) is known (1). This is because of the crossover in specific gravities for many oils at some point in weathering. Still, the various classes of oils tend to group themselves in certain specific gravity ranges. These are summarized in Table 18.

Table 18
Specific Gravity Ranges for Oils Studied

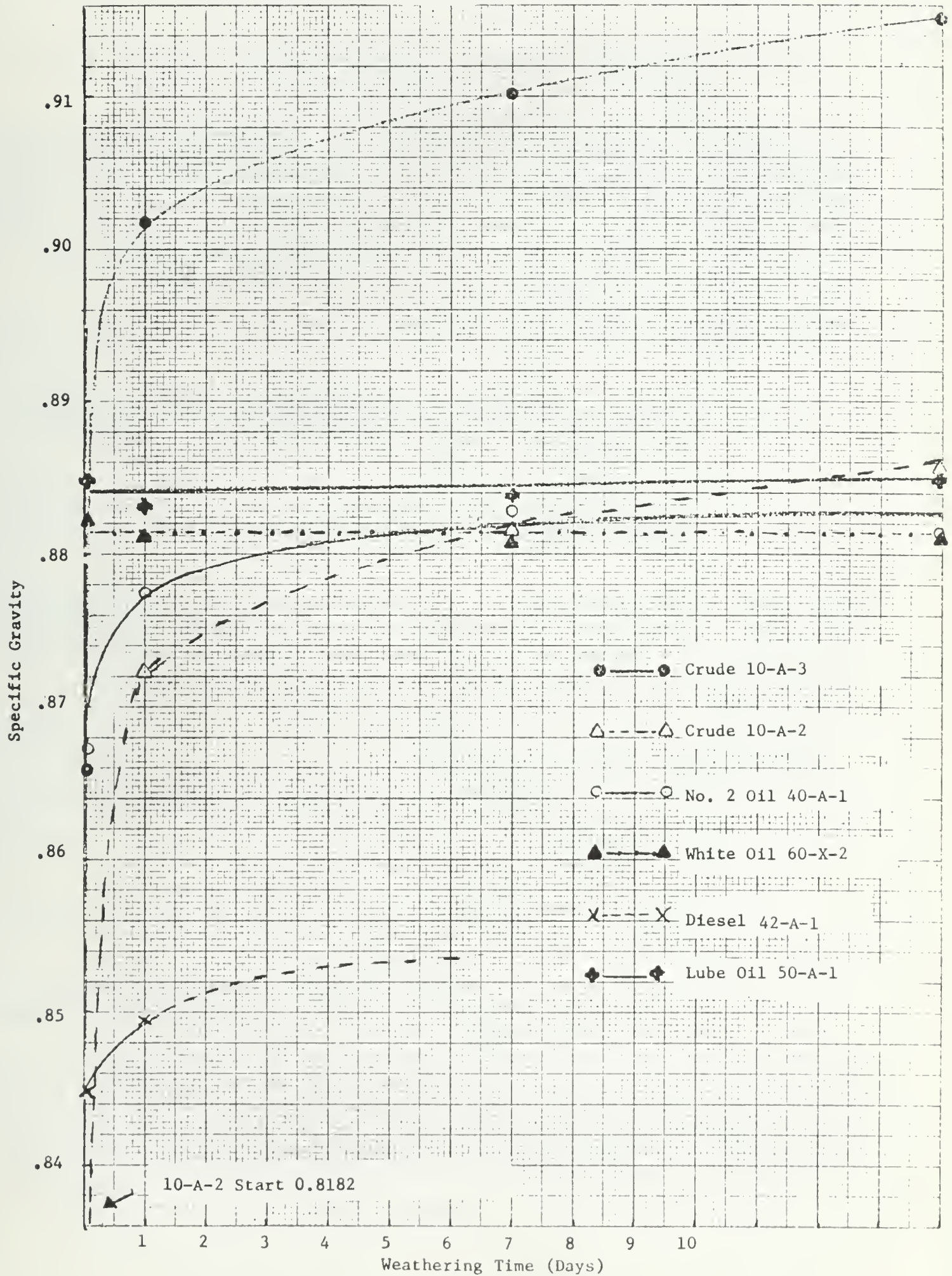
<u>Type of Oil</u>	<u>No. of Examples</u>	<u>Specific Gravity</u>			
		<u>Unweathered</u>		<u>Weathered (1)</u>	
		<u>Range</u>	<u>Median</u>	<u>Range</u>	<u>Median</u>
Crude	8	.8095-.9501	.8621	.8723-.9772	.9109
Blended Residual Fuels(2)	5	.8731-.9696	.9030	.8854-.9778	.9564
Distillate Fuels(3)	8	.8147-.8678	.8530	.8258-.8848	.8745
Lube Oils	4	.8795-.8865	.8841	.8794-.8857	.8830
White Oil	1	.8821	--	.8814	--
Gasoline	1	.7300			

(1) One day or more.

(2) Includes Bunker, No. 4, 5 and 6 Oils and Navy "special" fuel.

(3) No. 2 oil, diesel, gas oil and jet fuel.

Figure 12. CHANGES IN SPECIFIC GRAVITY WITH WEATHERING TIME



IV.2.1 Application of Specific Gravity Data to Fingerprinting

Specific gravity data may be useful in making broad classifications of spilled oil provided the suspect sample has weathered for a day or more. Thus, nearly all weathered crudes and residual fuels we have studied have specific gravities >0.8850 and most are above 0.9000 . None of the distillate fuels exceeds 0.8800 and the median value for weathered samples is 0.8745 . Lube oils fall in between distillate and heavy fuels but those we have examined so far cluster around 0.8840 (Table 18). Weathering has very little effect on the specific gravities of lube oils. Thus, it appears that two generalizations, based on the above may be drawn and cautiously applied.

- (1) If sample is known to have weathered for a day or more and has a specific gravity of .8800 or less it is very likely not a crude (or a highly unusual one) or a residual fuel.
- (2) Conversely, if the sample has a specific gravity of 0.90 or higher, it is almost assuredly not a distillate fuel such as No. 2 heating oil, diesel, gasoline, jet fuel, or lube oil.

Unfortunately, many exceptions to the above generalization exist (Appendix Table D1). In addition, specific gravities are tedious to measure and large samples are needed for conventional techniques. As a result, with the permission of the contract monitors, we discontinued this type of analysis in favor of other methods at this point.

IV.3 Gas Chromatographic Distillations

As originally pointed out (1), GC distillations may be useful in fingerprinting in three different ways:

- The GC trace is a crude fingerprint.
- The plots of boiling point vs percent distilled have characteristic shapes for many oils.
- Plots of specific gravity data vs some measure of average boiling points at different weathering times give characteristic straight lines.

These expectations have, in the main, been realized in cases where accurate GC distillation data could be obtained. The technique is most useful in the case of crude oils and light distillate products. Heavier materials, such as blended residual fuels do not always give satisfactory results.

IV.3.1 Effects of Weathering on Boiling Range Characteristics

Some selected G.C. distillation data from the first series of weathering experiments are shown in Table 19. These results are consistent with those obtained previously (1) if one allows for somewhat more rapid evaporation due to higher average temperatures and reduced slick thickness.

IV.3.2 Application of G.C. Distillation to Fingerprinting

We have pointed out (1) that the shape of the GC distillation curve, obtained by plotting the boiling points vs percent distilled may be characteristic for some types of oils. Such a plot for the six oils from Table 19 is given in Figure 13. A similar plot, on an expanded scale, is shown for the refined products in Figure 14. This type of analysis clearly distinguishes among certain broad classes of petroleum products. Curves from light fuels such as No. 2 heating oils and diesels are quite different from crudes or lube oils (Figure 13). Within these classes, differences are much less distinct. For example, curves for diesel and light heating oils and those for white oils and some lubes have quite similar shapes (Figure 14). An authentic sample of a similarly weathered sample would be required for identification. Crudes, as expected, tend to be more dissimilar (Figure 13 and Ref. 1). The effects of weathering on the GC distillation curves were examined in a previous project (1). The general shape of the curves are retained during the two week period.

The chromatograms from GC distillations may also be used as fingerprints (Figures 15-21). The resolution is, at least, sufficient to separate the oils into classes in many cases. The narrow boiling ranges of the refined oils (Figures 18-21) as compared to crudes and heavy fuels (Figures 15-17) are quite apparent. The light fuels (No. 2, Figure 6 and diesel, Figure 19) have mid points in their curves about 100°C lower than the heavier lube and white oils (20 and 21). An authentic sample, however, would be required to distinguish between a No. 2 heating oil and diesel or between a lube and a white oil. In this regard infrared and TLC are excellent supplementary tools. This is emphasized in Section V below. The two crude oils, 10-A-2 (Figure 15) and 10-A-3 (Figure 16) are readily distinguished because of the greater paraffinic character of the former (strong n-paraffin peaks throughout). The aromatic crude 10-A-3 exhibits greatly reduced paraffin peaks relative to the aromatic "envelope". It should be strongly emphasized that two "aromatic" crudes would have much more similar chromatograms and be harder to distinguish than 10-A-2 and 10-A-3. The bunker fuel (Figure 17) is interesting since it shows a bimodal distribution, peaking about 175°C and again at around 350°C. This indicates 20-A-1 is a blended residual fuel, (even though it was obtained as a straight run "bunker" fuel) containing much more light ends than might be expected for a heavy resid. After two weeks, much of the lighter material is gone (Figure 17B).

Table 19

Effect of Weathering on Boiling
Point Ranges of Various Oils⁽¹⁾

<u>Code No.</u>	<u>Type of Oil</u>	<u>Weathering Time</u>	<u>Percent Boiling Below</u>		
			<u>400°F</u>	<u>500°F</u>	<u>600°F</u>
10-A-2-0 ⁽²⁾	Crude	0	45	60	70
-I		24 hrs	2	17	40
-II		1 wk	--	2	25
-III		2 wks	--	--	20
10-A-3-0 ⁽²⁾	Crude	0	25	40	60
-I		24 hrs	<1	12	35
-II		1 wk	--	25	24
-III		2 wks	--	--	14
40-A-1-0	No. 2	0	19	51	88
-I		24 hrs	3	36	83
-II		1 wk	--	11	70(3)
-III		2 wks	--	2	60(3)
42-A-1-0	Diesel	0	5	24	87
		24 hrs	--	15	84
		1 wk	-----No Sample-----		
		2 wks			
50-A-1-0	Lube Oil	0	--	--	1.5
		24 hrs	--	--	1.5
		1 wk	--	--	1.5
		2 wks	--	--	1
60-X-2-0	White Oil	0	--	--	<1
		24 hrs	--	--	--
		1 wk	--	--	--
		2 wks	--	--	--

(1) "Standard" weathering conditions; average temp: 85°F.

(2) Zero hour results from previous runs [Ref. (1)].

(3) Very little material remaining.

Figure 13. GC Distillation Curves
for Some Oils Weathered
Two Weeks

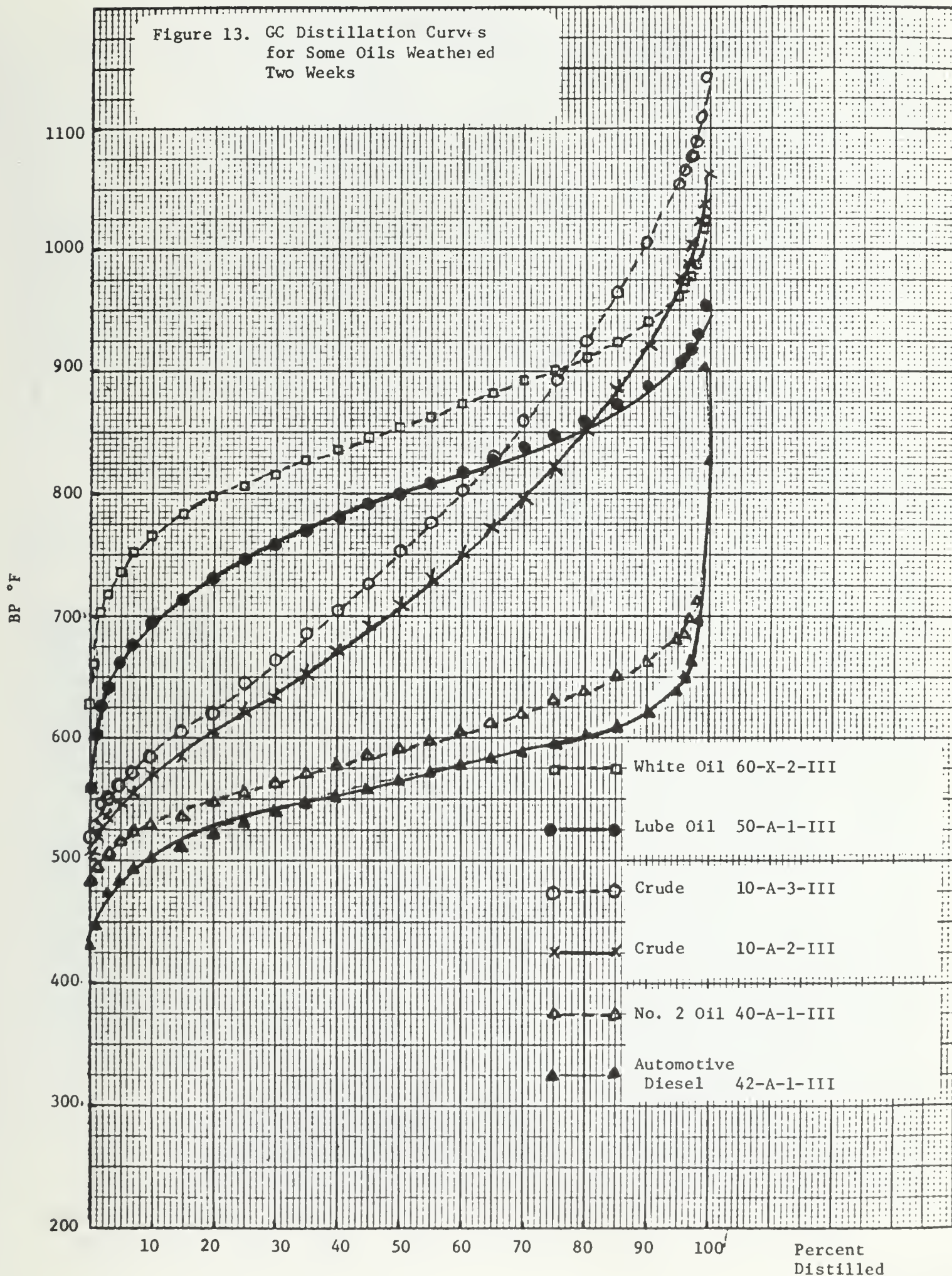


Figure 14. GC Distillations of Some
Refined Products
Two Week Weathering

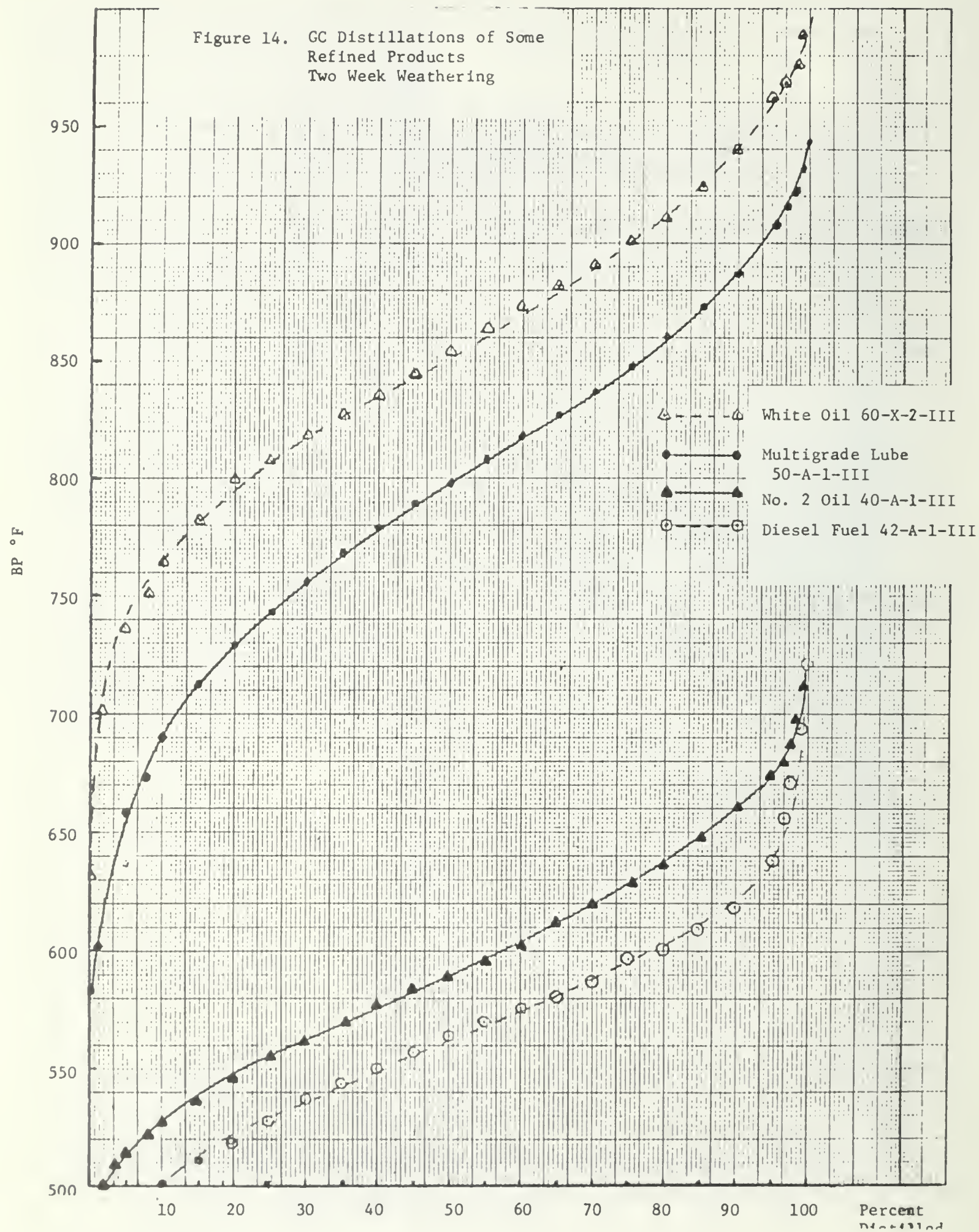


Figure 15. GC Distillation of Crude Oil 10-A-2

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.

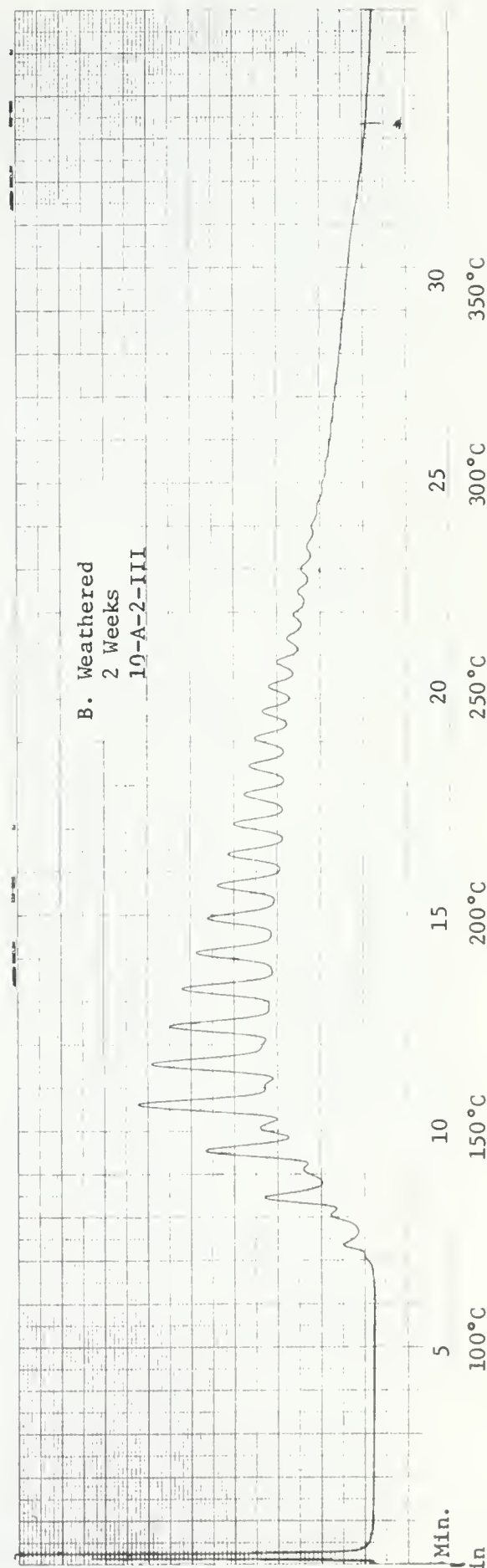
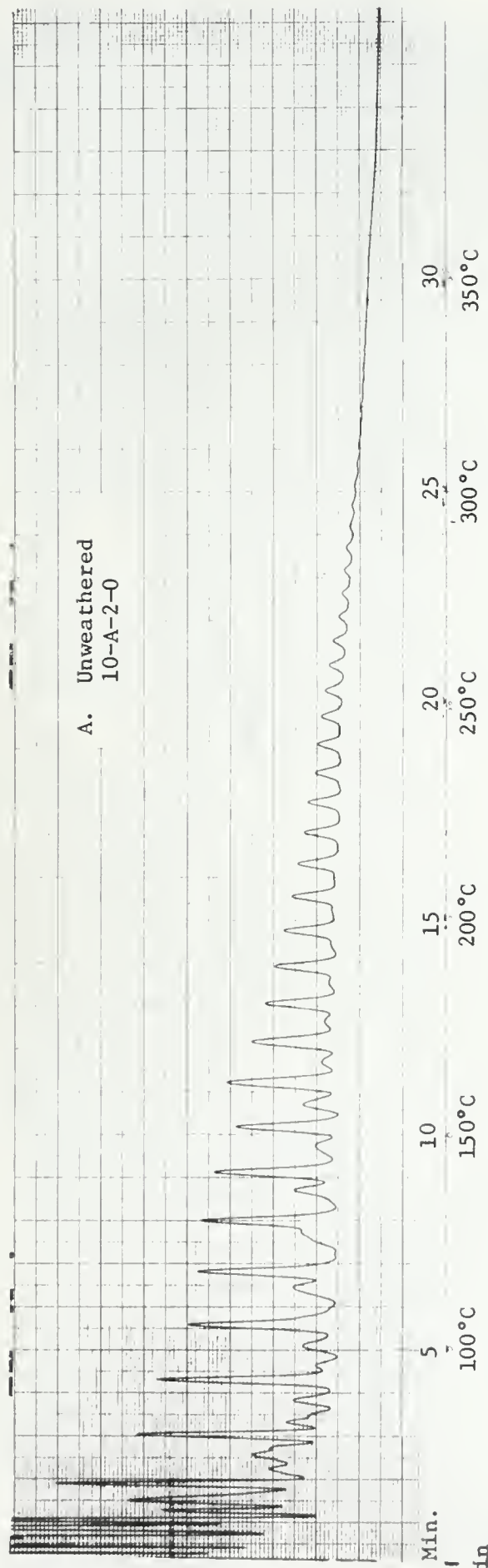


Figure 16, GC Distillation of Crude Oil 10-A-3

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.

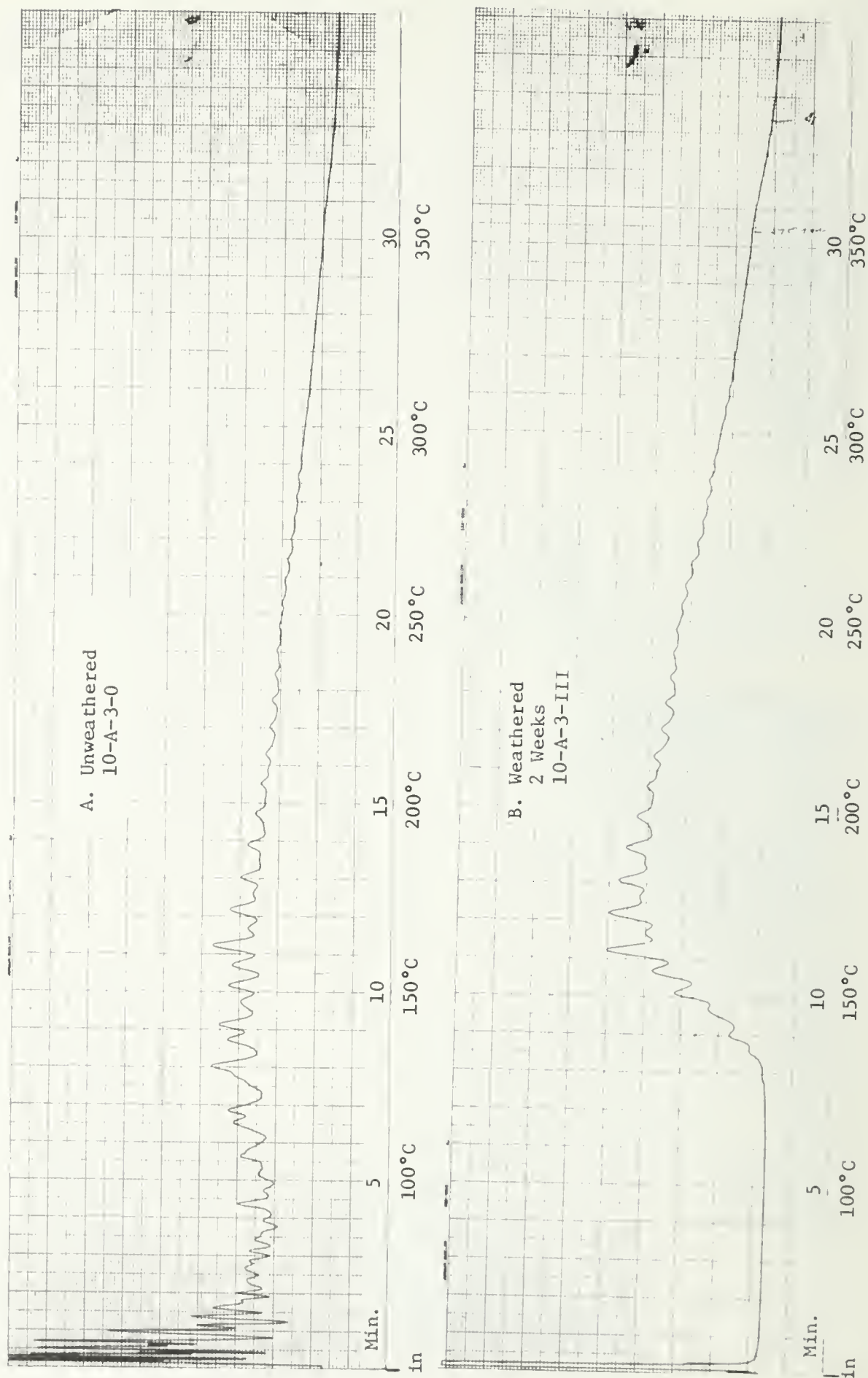


Figure 17. GC Distillation of Bunker "C" 20-A-1

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.

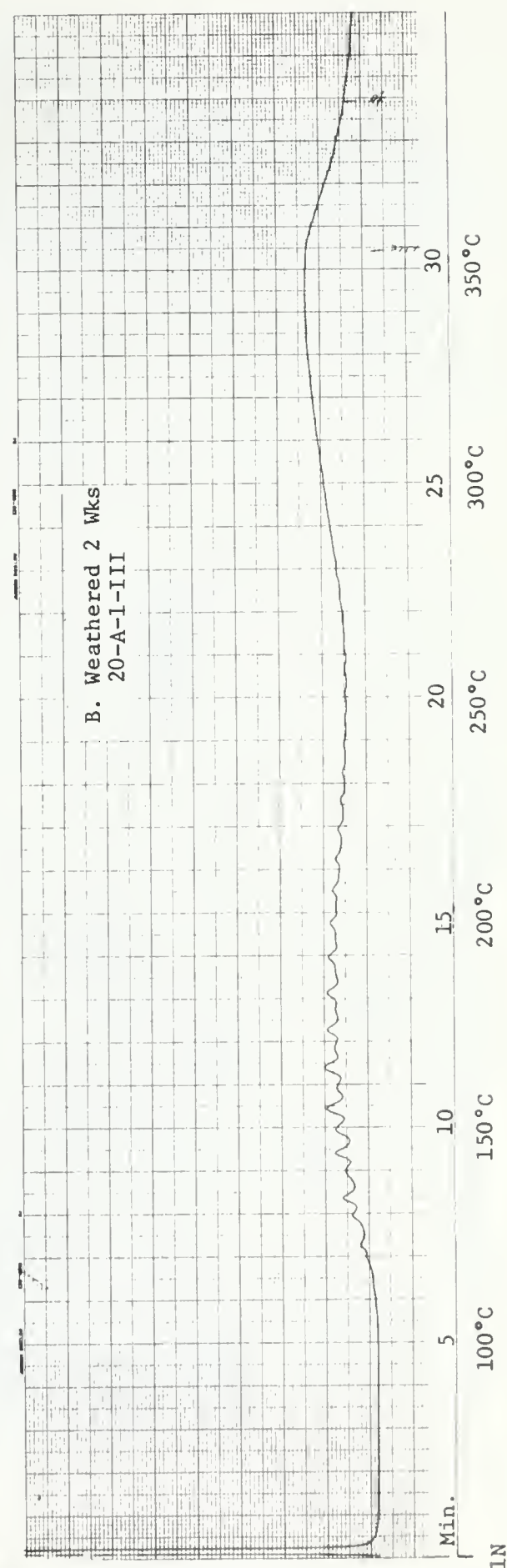
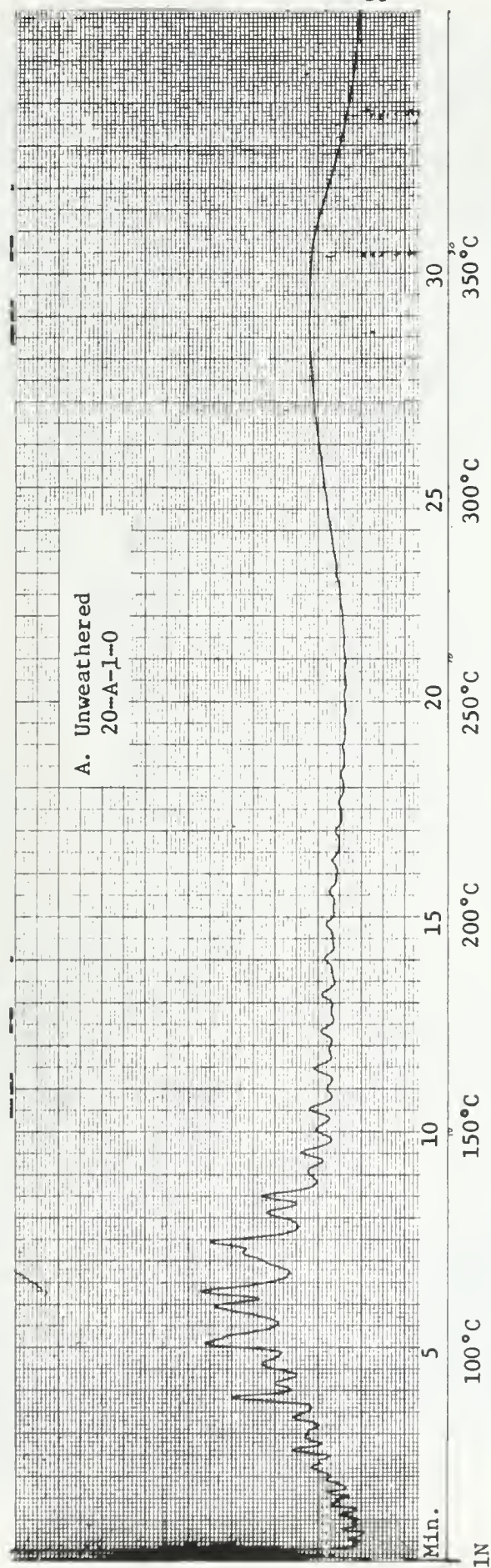


Figure 18. GC Distillation of No. 2 Heating Oil, 40-A-1

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.

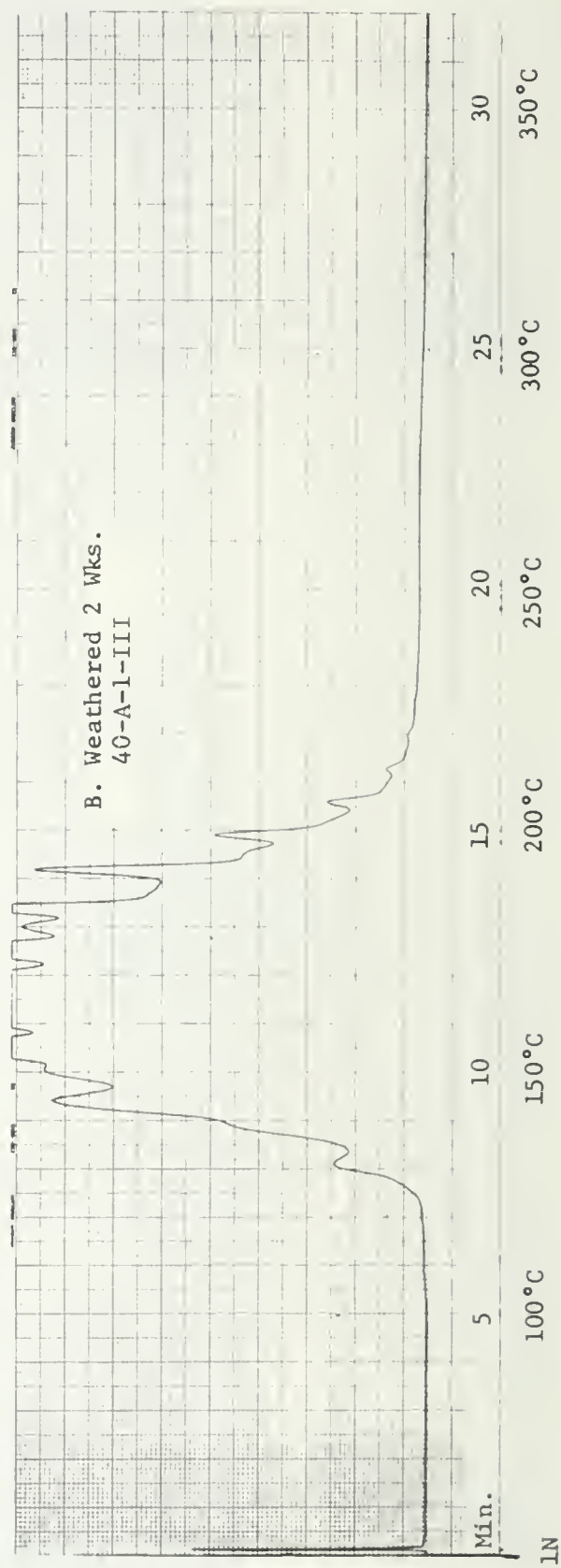
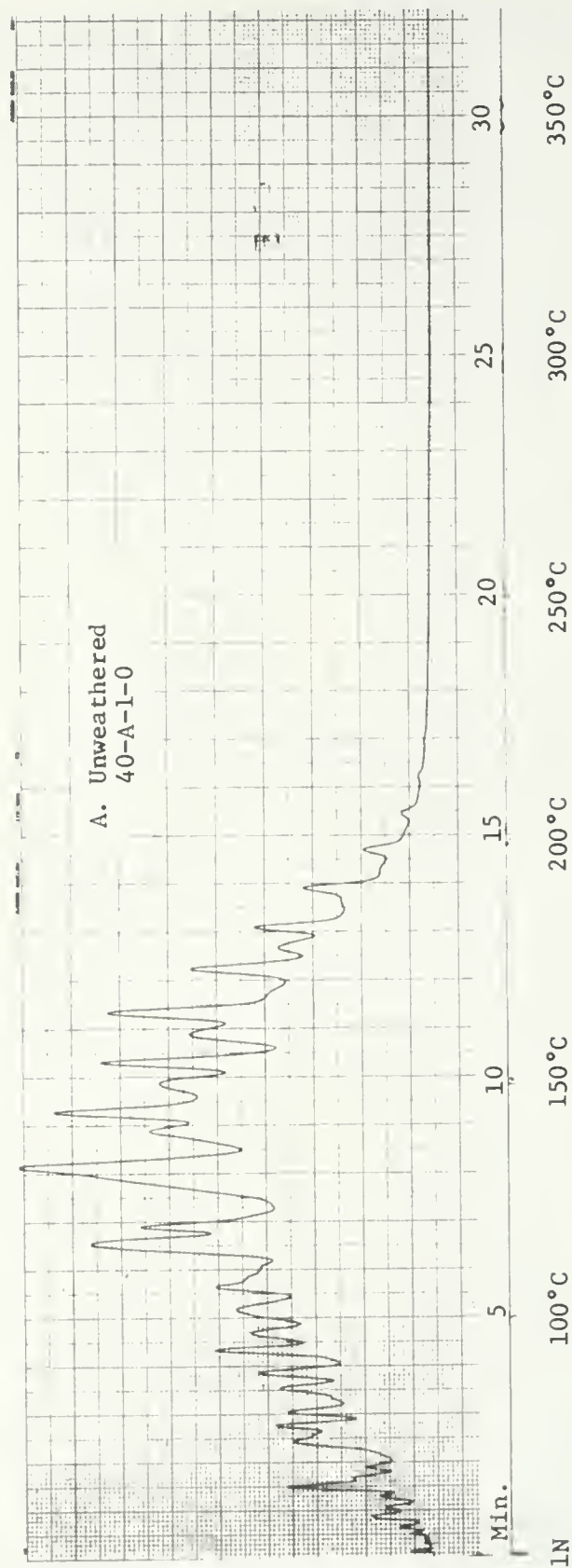


Figure 19. GC Distillation of Automotive Diesel 42-A-1

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.

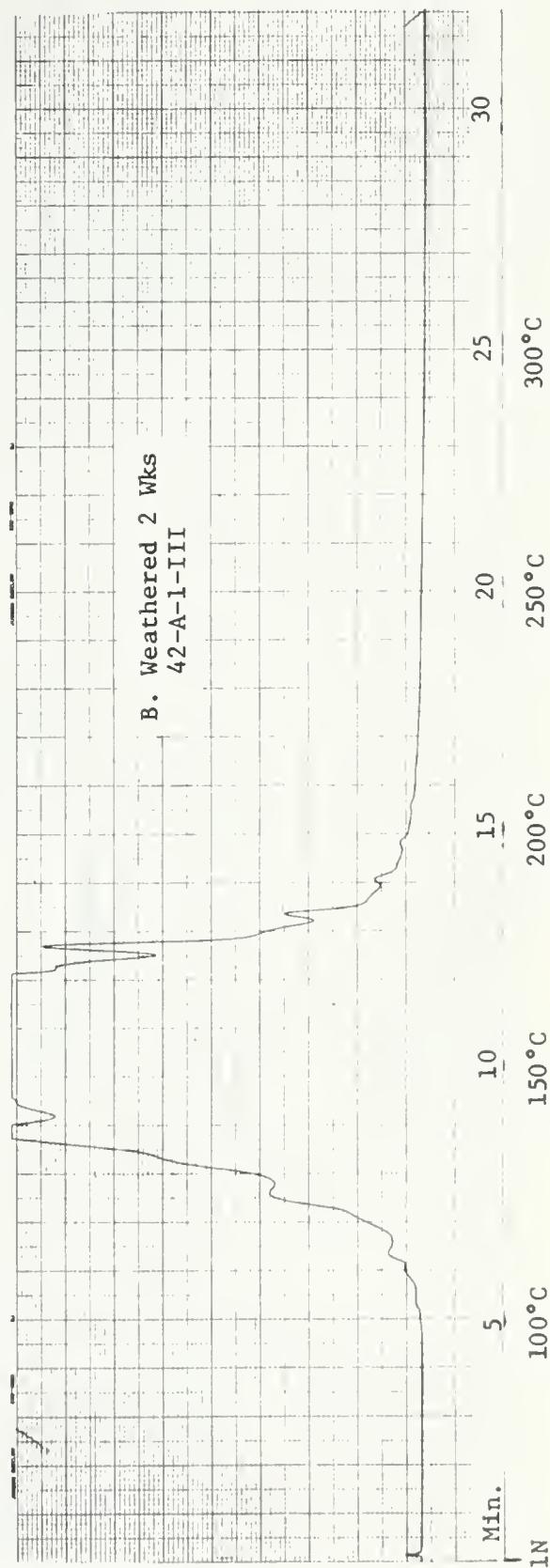
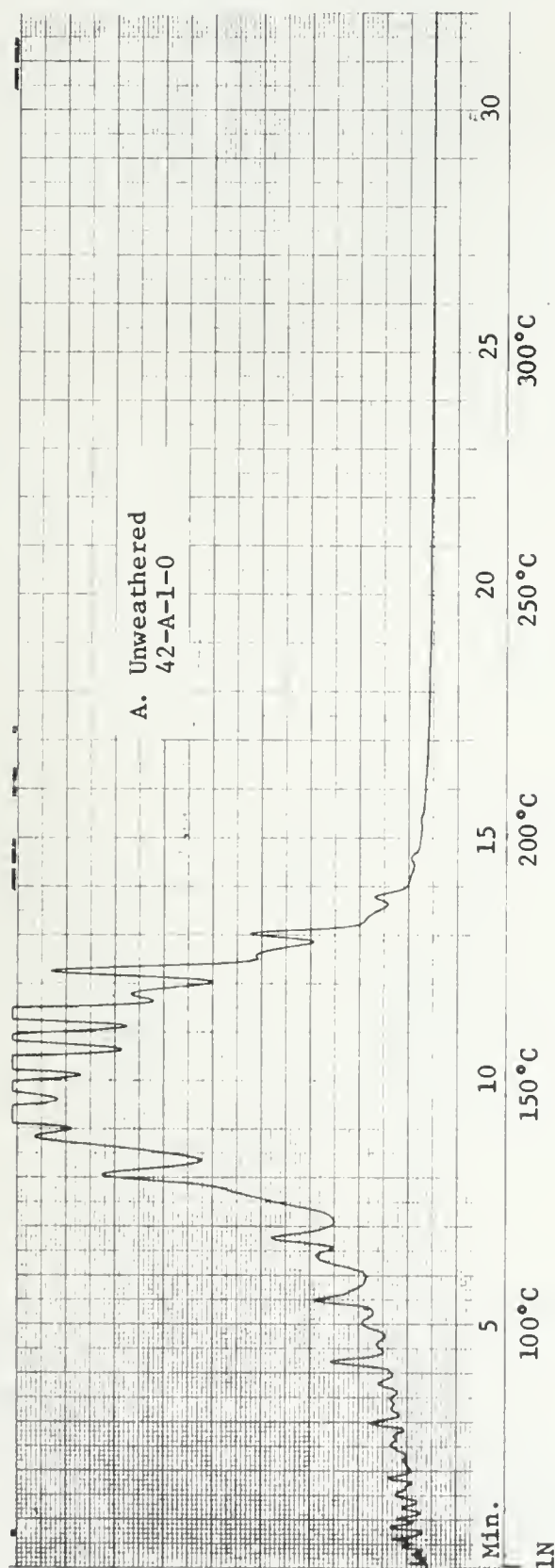


Figure 20. GC Distillation of Lube Oil 50-A-1

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.

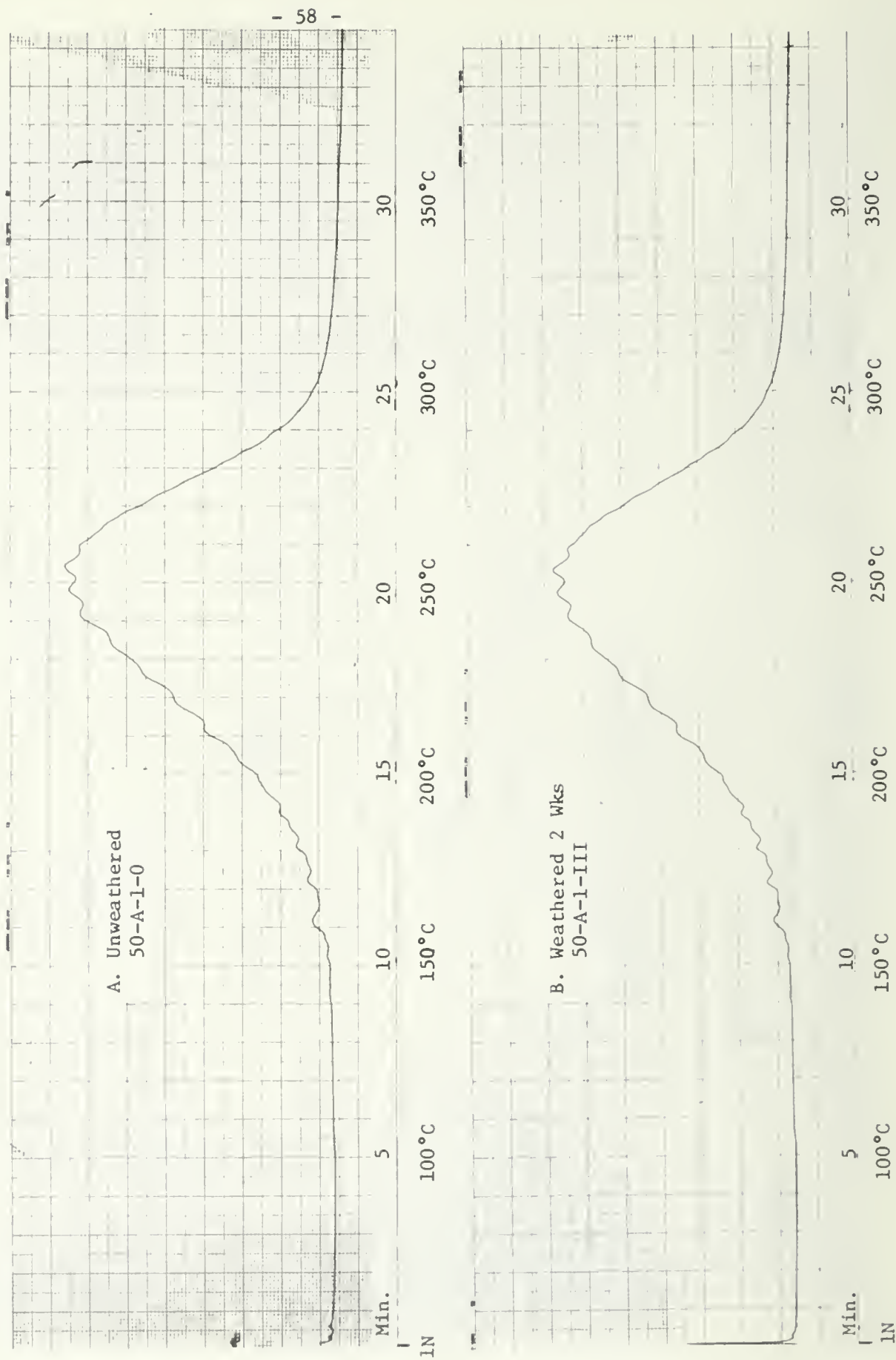
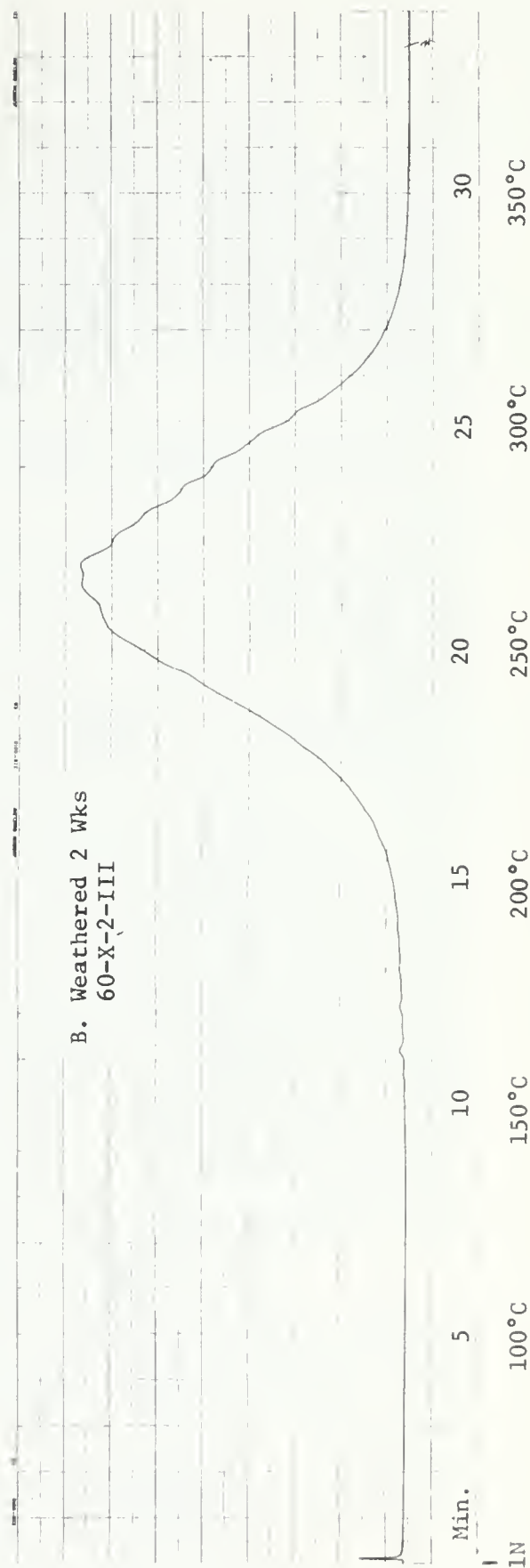
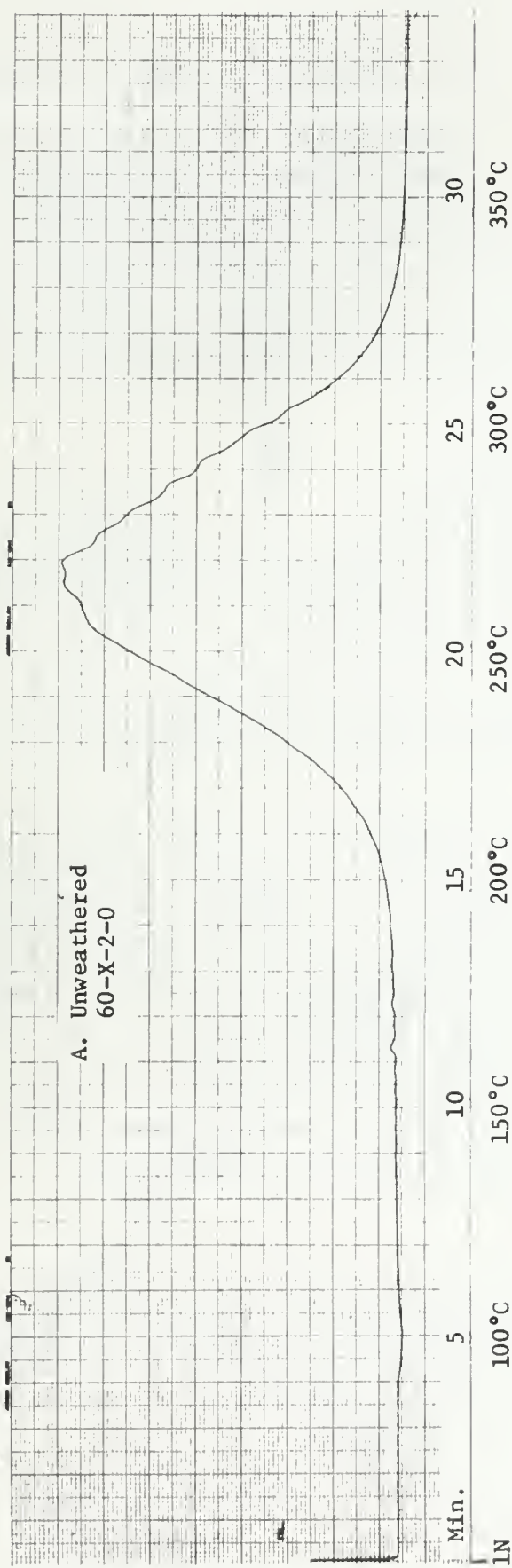


Figure 21. GC Distillation of White Oil 60-X-2

Column: 2', 1/4", W-98 on Chromasorb G

Program: 50°C - 375°C, 10°/min.

Chart Speed: 1"/min.



Thus, it appears that GC distillation may have some applications in fingerprinting (1,20). However, much the same results can be gleaned from the more highly resolved GC fingerprint traces (subsection IV.5.6 below). In addition, obtaining GC distillation data is somewhat tedious and expensive, requiring either calculations by hand or by computer analysis. Finally, as mentioned above, heavy materials do not afford good boiling range data. As a result, with the permission of contract monitors, we discontinued this work to apply the time and effort to liquid chromatography.

IV.4 Use of Combined Specific Gravity- G.C. Distillation Data

It was noted previously (1) that plots of specific gravity vs some measure of average boiling point for weathered samples afforded straight lines in the few examples studied. These lines had roughly parallel slopes in the case of petroleum products of similar class. This provides a potential identification tool for a suspect sample since weathering time need not be known. A potential pollution source could be eliminated if a plot of specific gravity vs average boiling point for the spill sample did not fall on or quite close to the standard curve for that oil.

Plots of specific gravity vs percent boiling <600°F (left scale or <500°F (right scale) for all samples for which both types of measurements have been obtained are shown in Figure 22. Again the linearity of the curves and parallel nature of the slopes of the two crudes and two distillate fuels is quite striking. As noted in Section IV.2, lube oils show virtually no change in either specific gravity or boiling ranges and show as a single point. A major disadvantage in this type of analysis is the need for extensive catalog of standard curves. These, in turn, call for large numbers of artificial weathering experiments and tedious routine analysis. As a result, we feel this method is less attractive than others and do not recommend including it as part of a fingerprinting system.

IV.5 Infrared Fingerprinting

In the hands of an experienced person, this technique is one of the methods of choice for identification of a pollution sample with that of a suspected source. No two samples have identical spectra although some practice in interpretation is useful especially if an artificially weathered, authentic sample is not available.

IV.5.1 Structural Assignments for The More Important Bands

The most important IR bands for fingerprinting purposes, along with the structural elements giving rise to them, are given in Table 20. Also shown are the classes of petroleum products in which each band is a major feature. These generalizations can be useful if interpreted carefully. A more complete discussion of IR characteristics is presented in subsection IV.5.3.

Figure 22. Plots of Specific Gravity vs. Average Boiling Point for Some Petroleum Products During Weathering

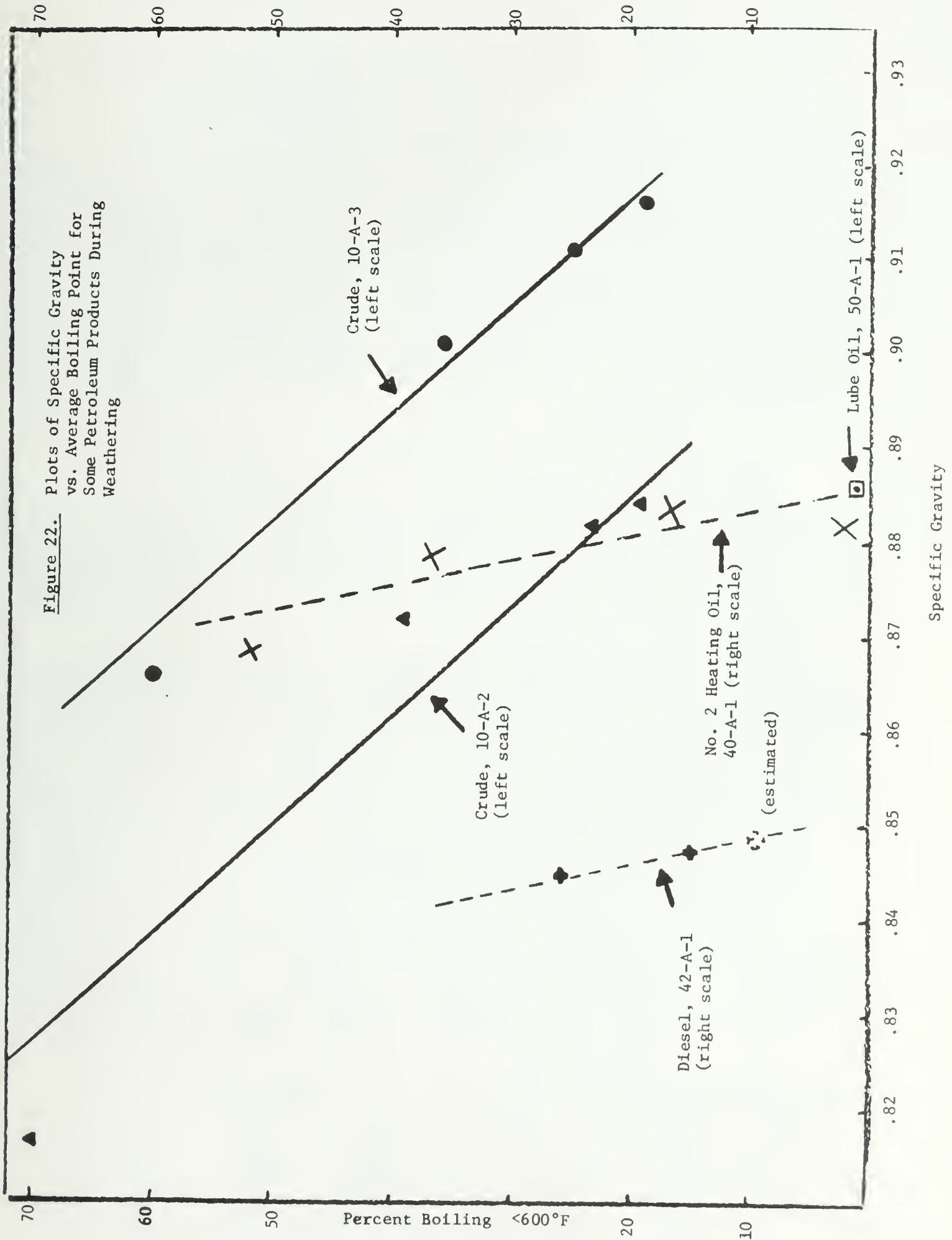


TABLE 20

STRUCTURAL ASSIGNMENTS FOR IMPORTANT
IR BANDS IN PETROLEUM PRODUCTS(1,2)

Frequency (cm ⁻¹)	1740	1700	1600	1460	1375	1235	1030	1010	970	870	815	745	725	695	680	675
Structural Assignment	C ⁰ (Ester)	C ⁰ (acid ketone)	C-C (Aromatic)	-CH ₃	-CH ₃	?	Ar-H	?	C-H (Alicyclic)	Ar-H	Ar-H	Ar-H	-CH ₂ -	Ar-H (Monosubst)	?	Benzene
Crudes																
Unweathered			X	X	X		X		X	X	X	X	X	X		X
Weathered		X(3)	X	X	X		X		X	X	X	X	X	X(3)		
Residual Fuels (Blended)																
Unweathered			X	X	X		X		X	X	X	X	X			
Weathered		X(3)	X	X	X		X		X	X	X	X	X			
Diesel Fuels																
Unweathered			X	X	X		X		X	X	X	X	X			
Weathered		X(3)	X	X	X		X		X	X	X	X	X			
No. 2 Heating Oils																
Unweathered			X	X	X		X		X	X	X	X	X	X		
Weathered		X(4)	X	X	X		X		X	X	X	X	X	X(3)		
Gasoline			X	X	X		X		X	X	X	X	X	X		X
Lube Oils																
Unweathered	X(5)	X(5)		X	X(5)	X	X(6)		X	X(3)	X(3)	X	X		X(6)	
Weathered	X(5)	X(5)		X	X(5)	X	X		X	X	X	X	X			
White Oils				X	X		X		X				X			

(1) Ref. 30; center point of ranges is given..

(2) The familiar bands from 3030-2825 cm⁻¹ due to C-H stretching modes are of relatively little use and are not included.

(3) Weak; may be observed in some cases.

(4) Strong band in many weathered heating oils due to oxidation of olefins.

(5) Bands due to additives vary from product to product.

(6) Due to water soluble additive--lost on weathering.

IV.5.2 Effects of Weathering Time on IR Spectra

Two full sets of IR curves are shown in Figures 23 and 24. The changes in the crude oil spectra (Figure 23) are quite typical for crudes. Rapid loss of the light aromatics in the 650 cm^{-1} - 700 cm^{-1} region and of the sharp peak at 765 cm^{-1} occurs. Similar effects are seen in the heating oil spectra (Figure 24) except that the changes occur more slowly. This is because heating oils have many of the lightest aromatics already removed by distillation (note absence of benzene band at $670\text{--}675\text{ cm}^{-1}$). At any rate, most obvious weathering changes occur during the first week and the spectra of one and two week samples are quite similar. One area of the spectrum which does continue to change in certain cases is the carbonyl band at 1700 cm^{-1} . This increases steadily with time for No. 2 fuel oil 40-A-1, for example (Figure 24).

IV.5.3 Use of IR in Classifying Petroleum Products

Some typical spectra for various classes of petroleum products are shown in Figures 25-33. Only the extreme cases, unweathered and weathered two weeks are shown to facilitate comparisons. Spectra have also been run at one-day and one-week intervals for all samples except the automotive diesel for which no one-week sample was obtained.

All the samples have characteristic spectra which are still recognizable after two-weeks weathering. The two crudes in this series (Figures 25 and 26) are quite different in composition and this is apparent from the traces. The first example, 10-A-2 is a light, paraffinic crude. It shows a strong paraffin band at 725 cm^{-1} and weaker aromatic bands at 745 cm^{-1} , 820 cm^{-1} , $870\text{--}880\text{ cm}^{-1}$, 1020 cm^{-1} and 1610 cm^{-1} (Figure 25A) (30,31). This general pattern is retained after weathering (Figure 25B). Missing, however, in the weathered sample are bands at 675 and 695 cm^{-1} attributable to the volatile aromatics (31) which are rapidly lost (1). The second crude, 10-A-3, is heavier and more aromatic (relative intensities of aromatic vs paraffinic bands in Figures 26A and 26B). The heavier crude, 10-A-3, is also somewhat more susceptible to oxidation (build up of band at 1710 cm^{-1} , Figure 26B) as might be expected from a more aromatic material (1). Both unweathered samples (Figures 25A and 26A) are readily classified as crudes since they show light aromatics as well as the broad bands in the $700\text{--}900\text{ cm}^{-1}$ region; bands from refined products are much better resolved. However, the weathered materials, while clearly different, could not be differentiated from resids or blended resids without an authentic sample.

The bunker sample (20-A-1, Figure 27) is identified as a residual fuel or a heavily weathered crude by the broad, poorly resolved bands in the $700\text{--}900\text{ cm}^{-1}$ region. It is quite clearly not derived from either of the crudes just described. The spectrum of the bunker changed very little during weathering (Figures 27A and B) although some increase in the intensity of the band at 1030 cm^{-1} is apparent.

FIGURE 23. IR SPECTRA OF CRUDE 10-A-2

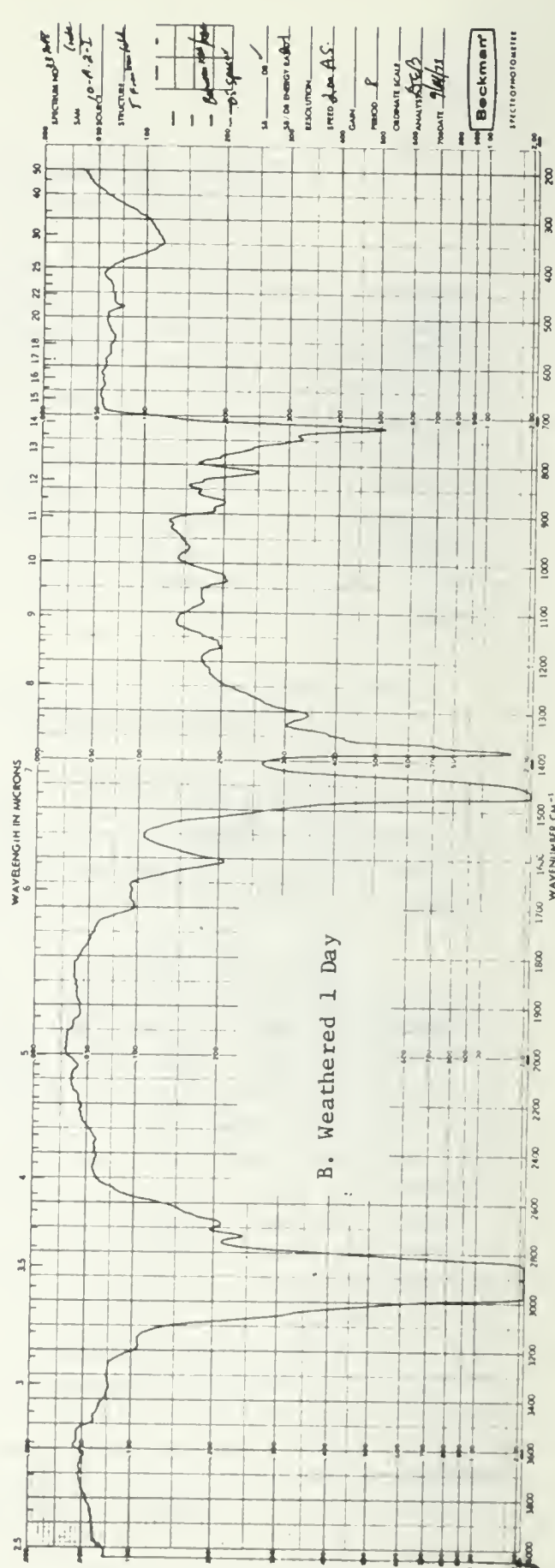
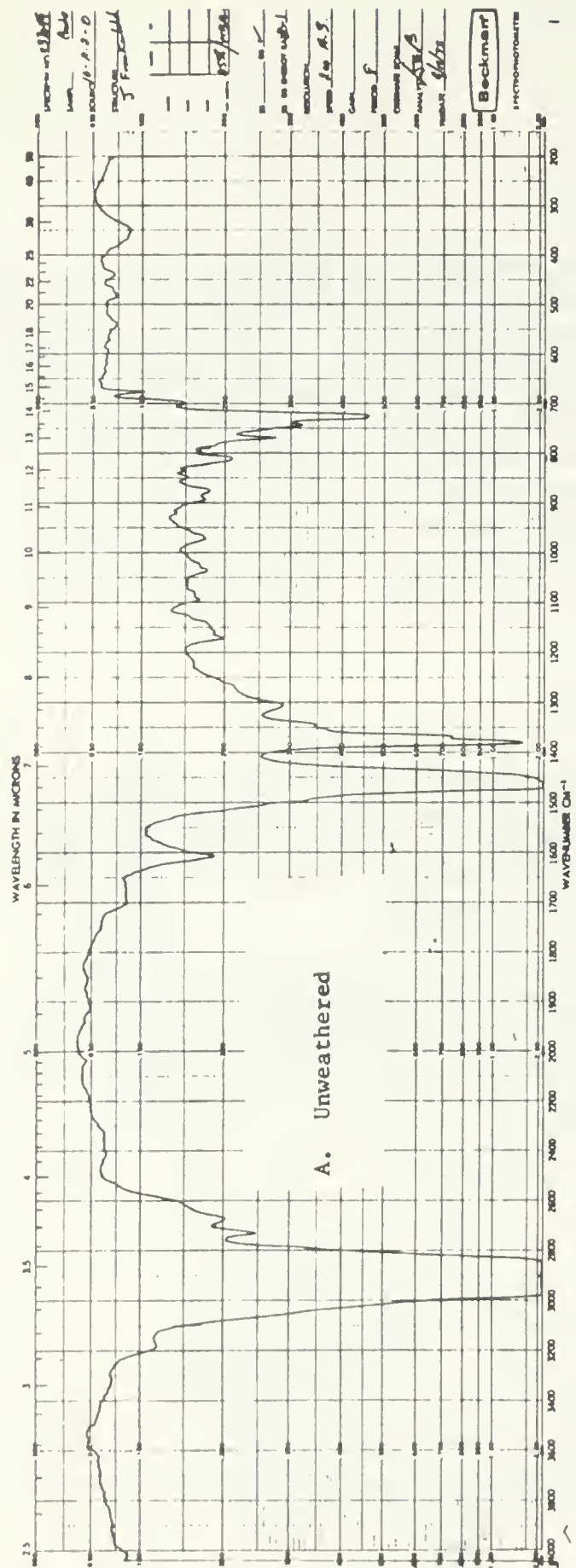


Figure 23 (Cont'd.)

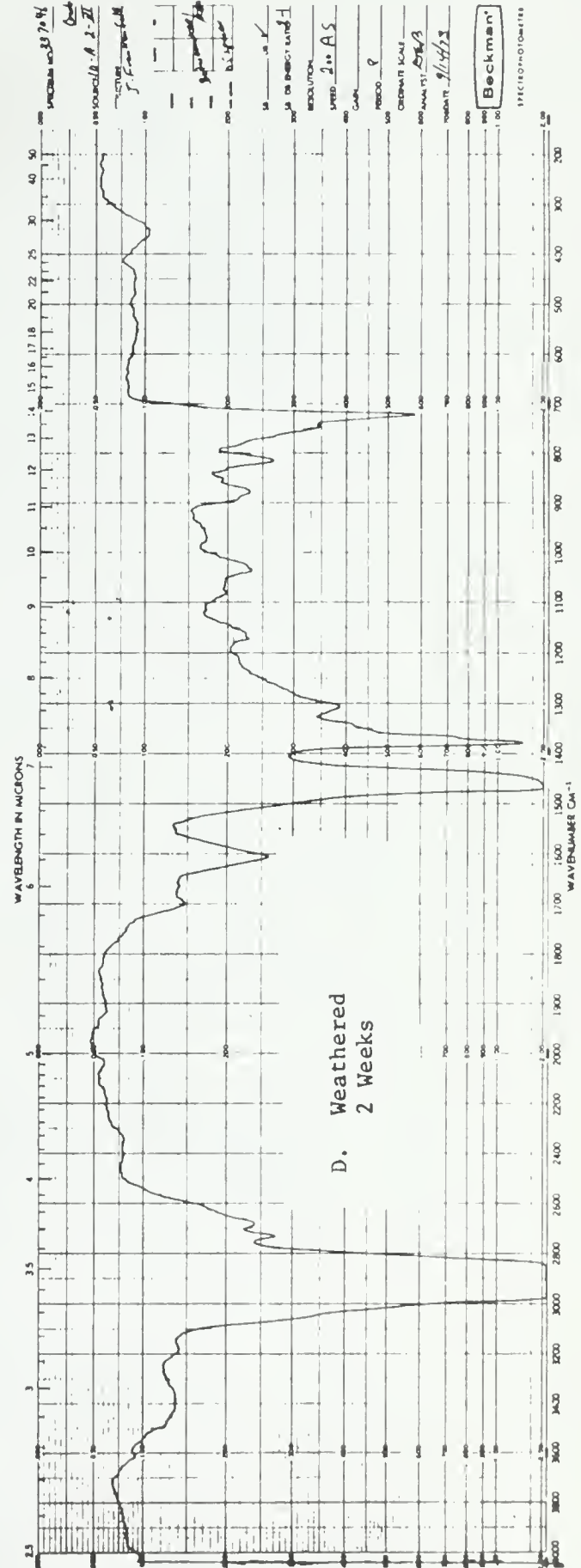
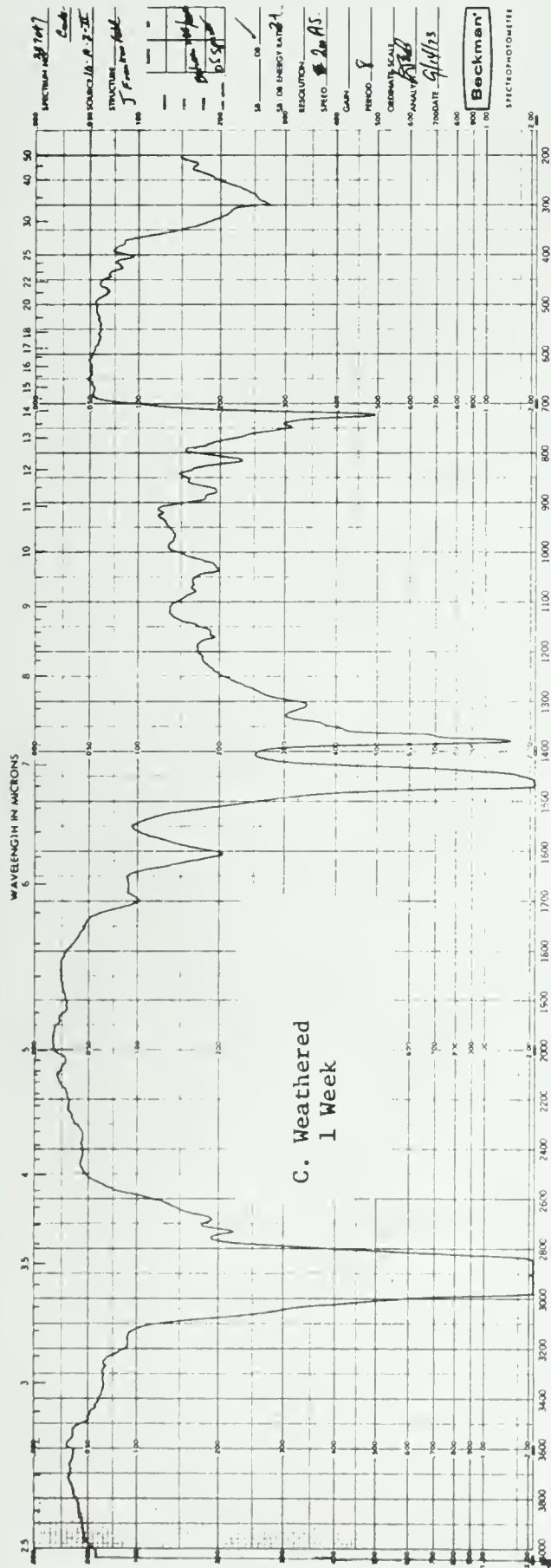


FIGURE 24. IR SPECTRUM OF NO. 2 HEATING OIL 40-A-1

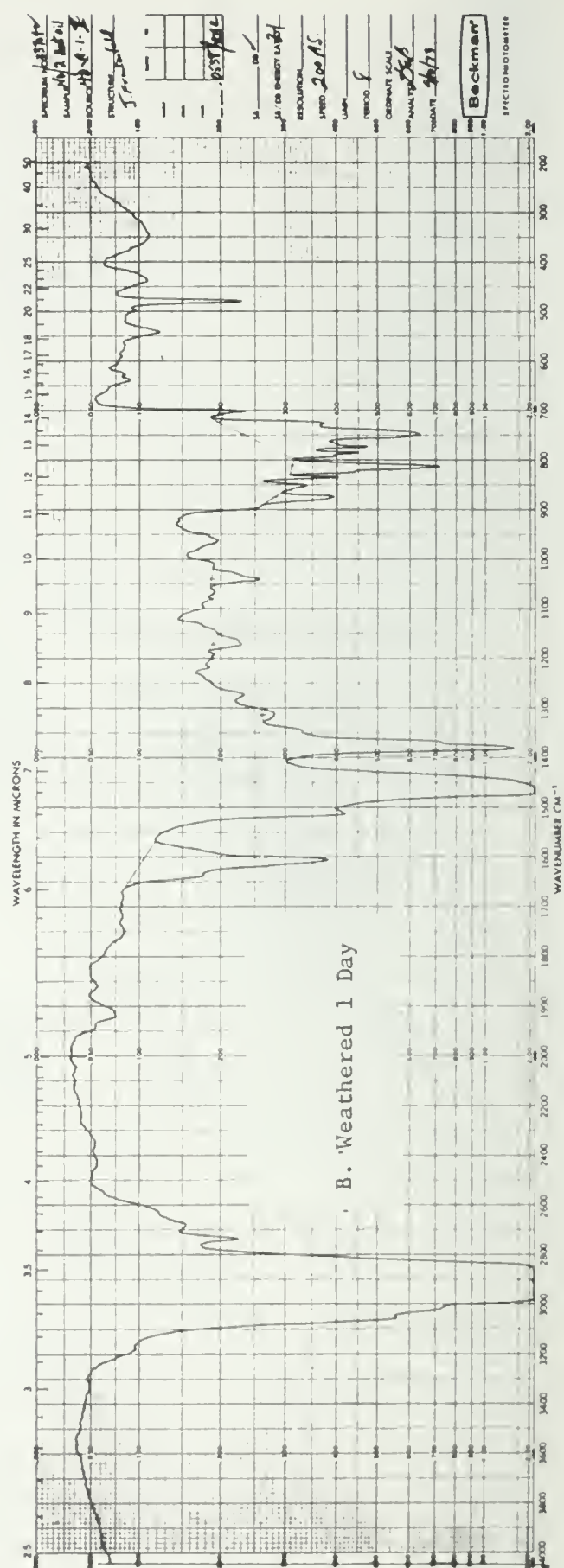
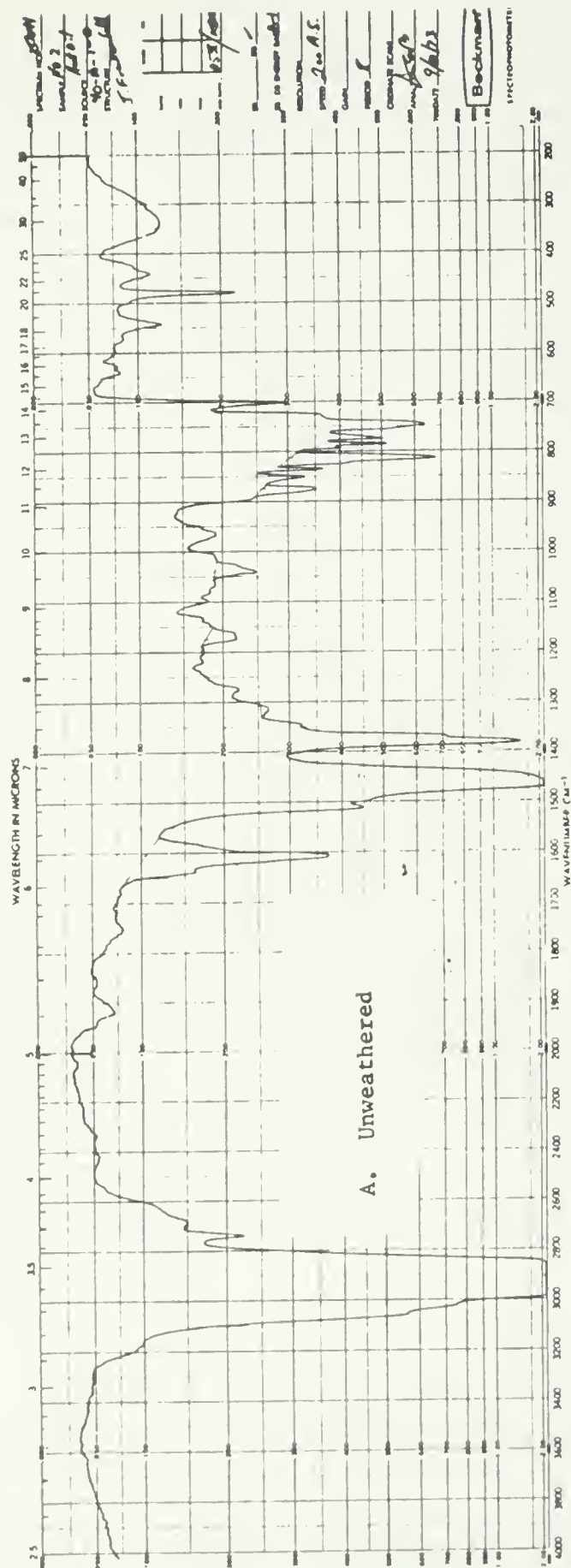
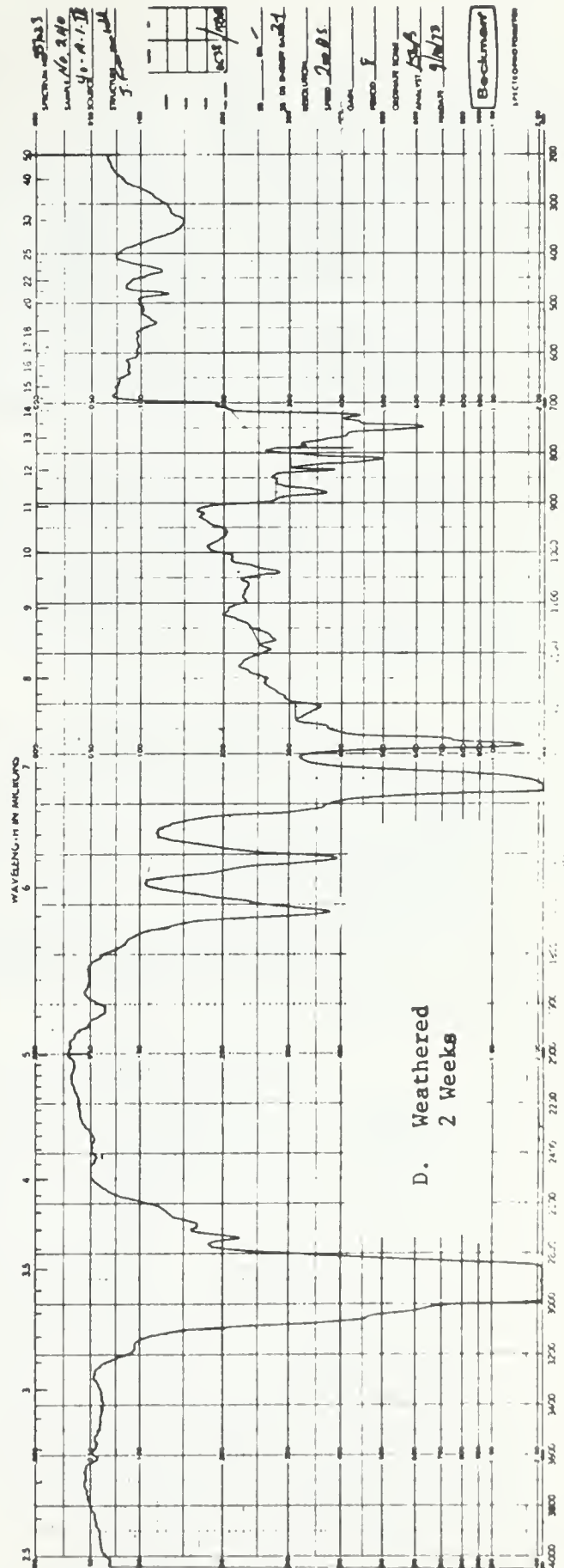
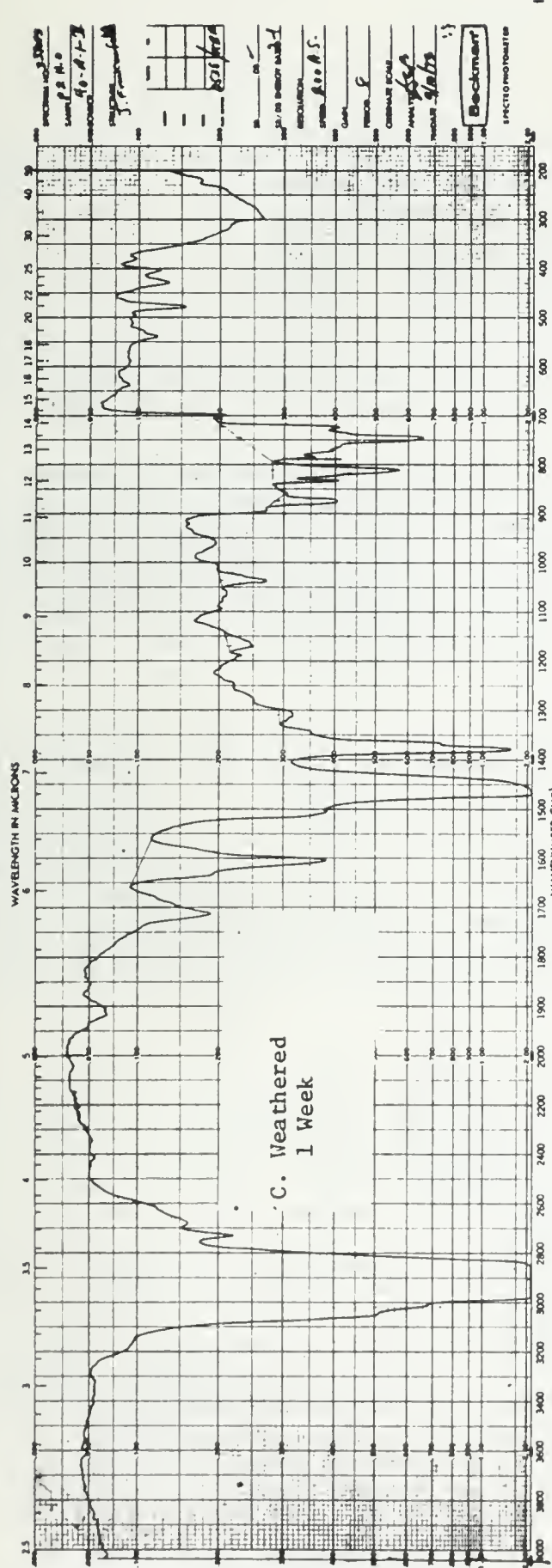


FIGURE 24 (Cont'd.)



The two distillate fuels (Figures 28 and 29) exhibit a highly resolved series of 8-10 bands in the $700\text{--}900\text{ cm}^{-1}$ region. This characteristic pattern is still discernable after weathering, especially with the No. 2 fuel oil (Figure 28B). Significantly, these two refined products are clearly distinguishable from each other. In fact, the spectrum of weathered diesel is much more similar to that of the weathered paraffinic crude 10-A-2 (compare Figures 25B and 29B). However, there are ample differences in the ratios of the $725\text{--}745\text{ cm}^{-1}$ bands and in the bands in the $900\text{--}1200\text{ cm}^{-1}$ region for separating the diesel from the crude oil.

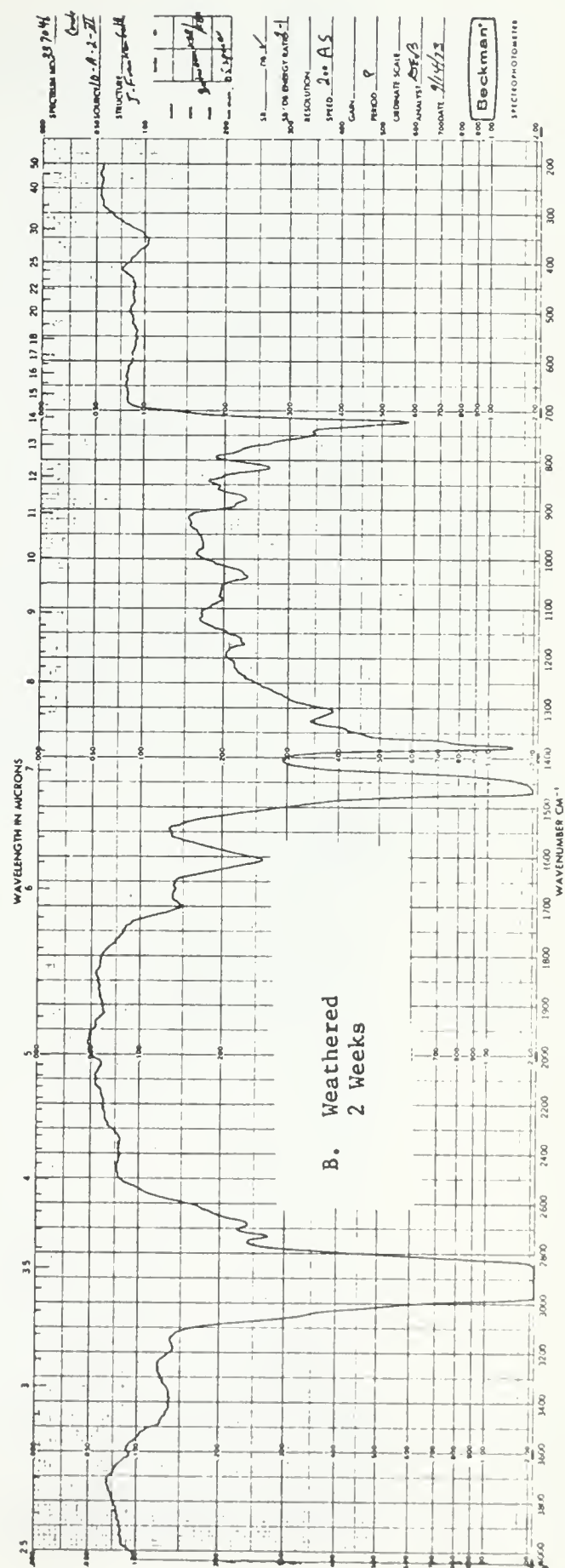
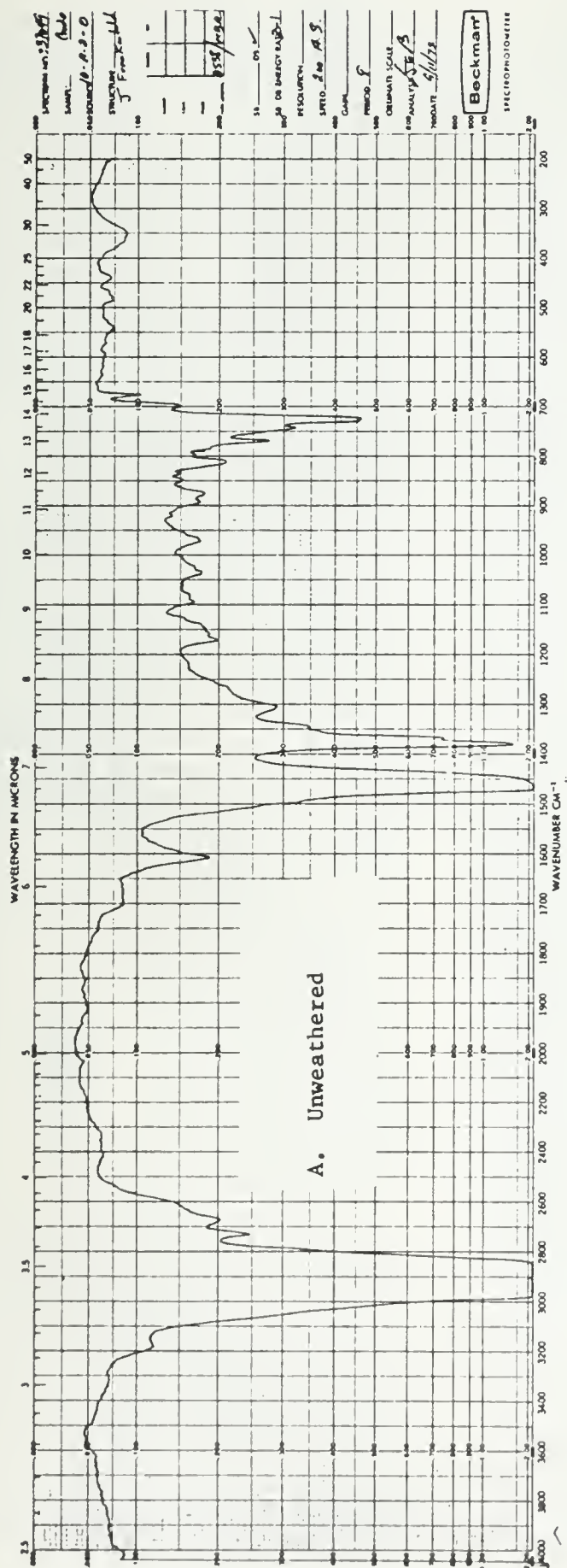
A very significant feature of the weathered No. 2 heating oil is the strong band at 1700 cm^{-1} (Figure 28A), not present in the unweathered material (Figure 28B). This indicates extensive oxidation, far greater than observed with any of the other oils. As pointed out before (1) this is indicative of the presence of easily oxidized groups, probably activated aromatic and olefinic species in the original sample. Diesels have fewer of these.

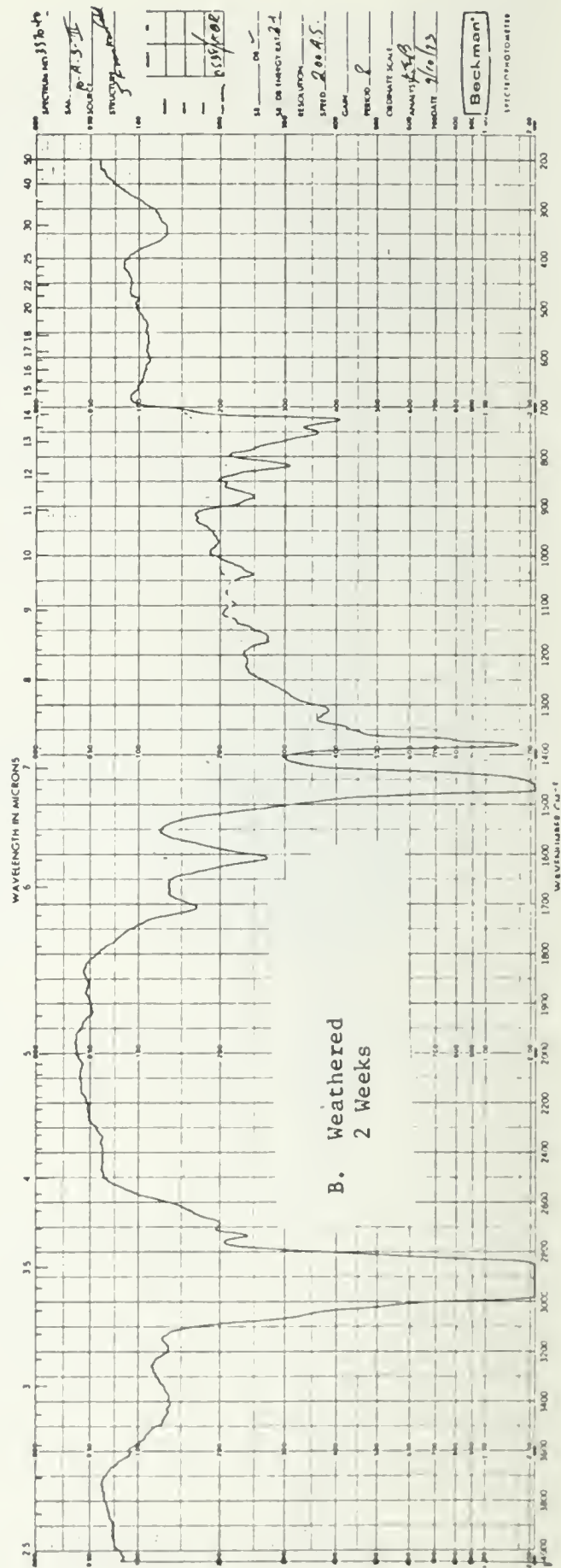
The spectra for two highly refined, very light distillate fuels are shown in Figures 30 and 31. Because of their extreme volatility, only unweathered and/or one-day samples could be obtained. The gasoline (Figure 30) shows typical, highly resolved bands in the $675\text{--}835\text{ cm}^{-1}$ region and could hardly be confused with any other products. Noteworthy are strong bands at 675 cm^{-1} and 695 cm^{-1} (benzene and monosubstituted aromatics). The gasoline is also more aromatic in general than jet fuel (stronger band at 1600 cm^{-1}). Jet fuel, being of the kerosene type, would be difficult to distinguish from light diesels, or other kerosenes especially when weathered.

The spectra of the lube oils show interesting and unique features. The bands at 675 cm^{-1} , 1010 cm^{-1} and 1235 cm^{-1} (Figure 32A) are not seen in any of the other samples. These are ascribable to additives in the oil. The large band at 1710 cm^{-1} in the unweathered lube, (Figure 32B) is also likely due to the presence of additives. The bands at 675 cm^{-1} and 1010 cm^{-1} disappear quickly on weathering (Figure 32B), probably by dissolution in the aqueous phase. The absorption at 1235 cm^{-1} remains, however, and serves as an excellent indication of a lube oil. The 1235 cm^{-1} band may be ascribed to a branched polyolefin used in many lubes as a viscosity modifier. Since various manufacturers use different additives, the bands attributed to them may prove useful in identifying the particular sample as well as typing it as a lube oil. Another important feature of this lube is its low aromaticity (weak absorptions at 1610 cm^{-1} , 810 cm^{-1} and 745 cm^{-1}). Next to the white oil it appears to be the least aromatic in character of all samples studied so far.

The major feature of the spectra of the white oil, 60-X-2, is the complete lack of aromatic bands. A cursory glance at the spectrum of an unknown material would establish that, if petroleum derived, it must be of the white oil type.

It seems clear that infrared spectroscopy is a valuable tool for classifying types of petroleum products. Its principal use, however, is in identification as discussed in the following subsections.





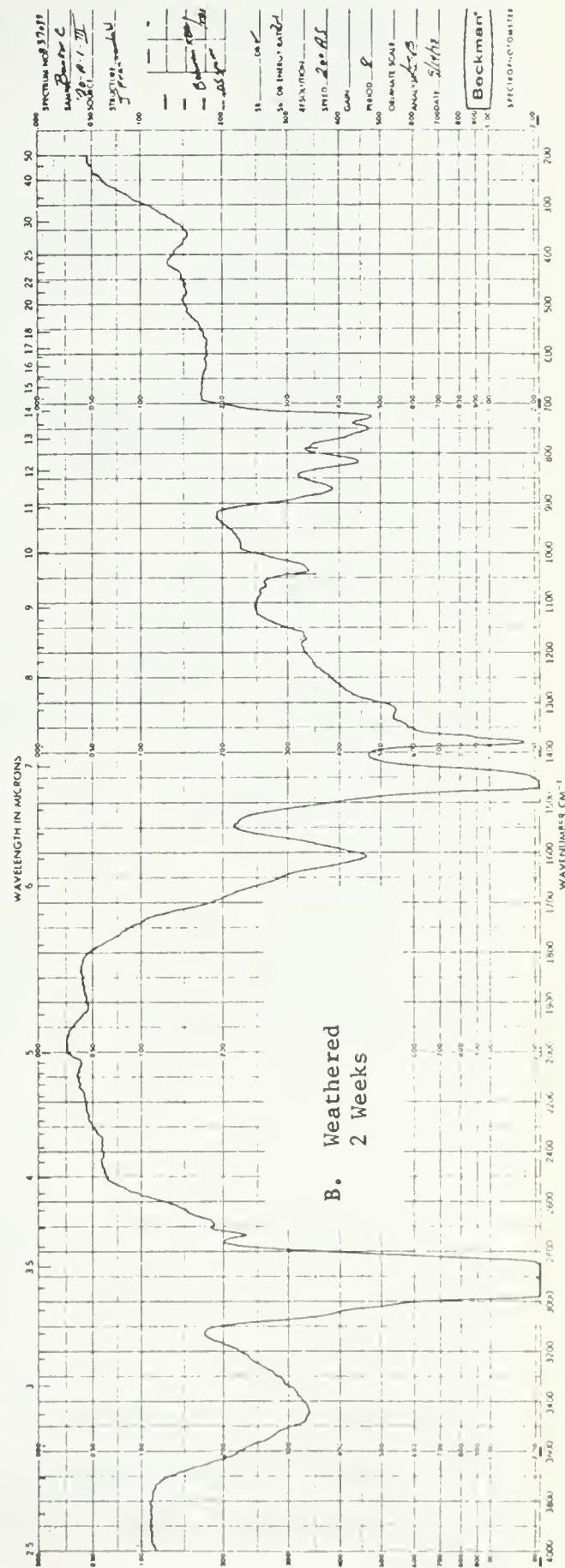
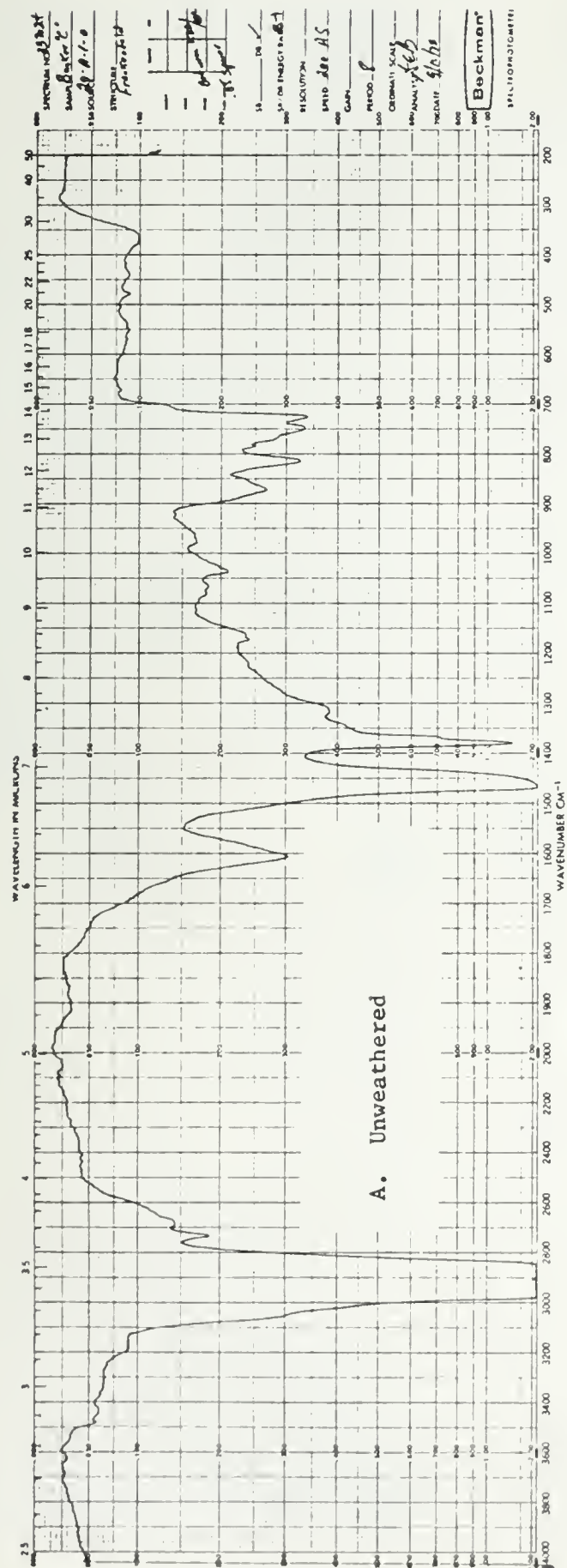


FIGURE 28. IR SPECTRA OF NO. 2 HEATING OIL 40-A-1

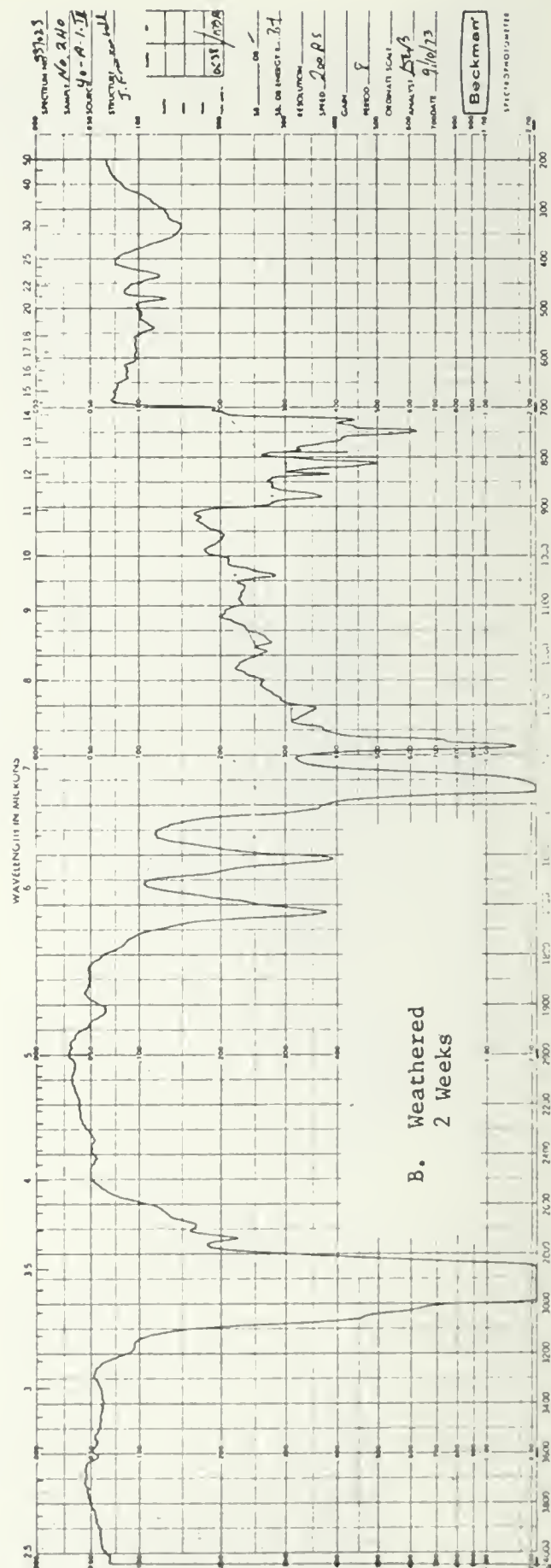
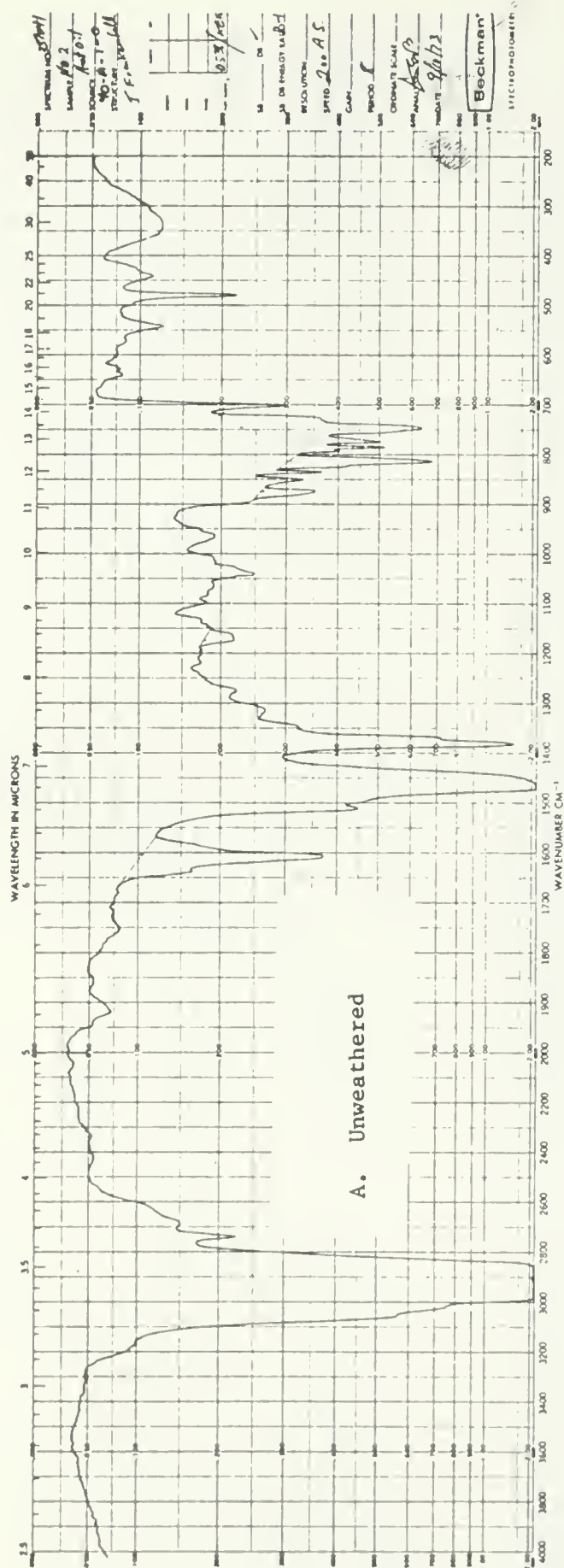


FIGURE 29. IR SPECTRA OF AUTOMOTIVE DIESEL 42-A-1

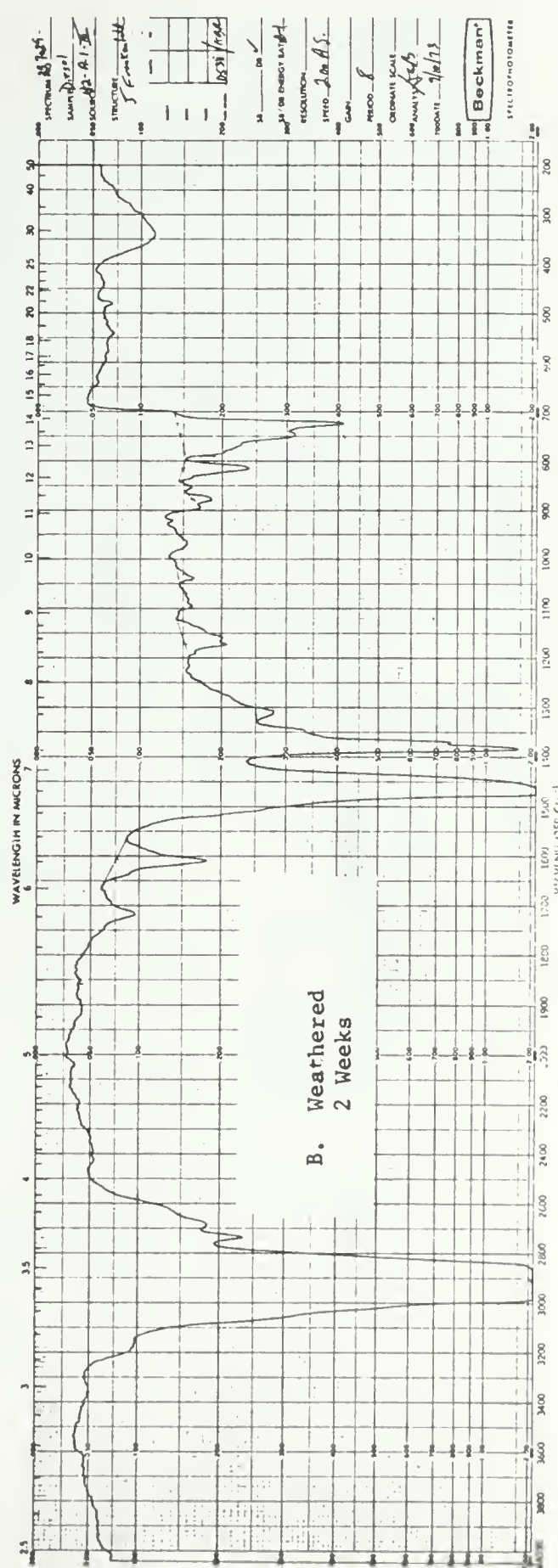
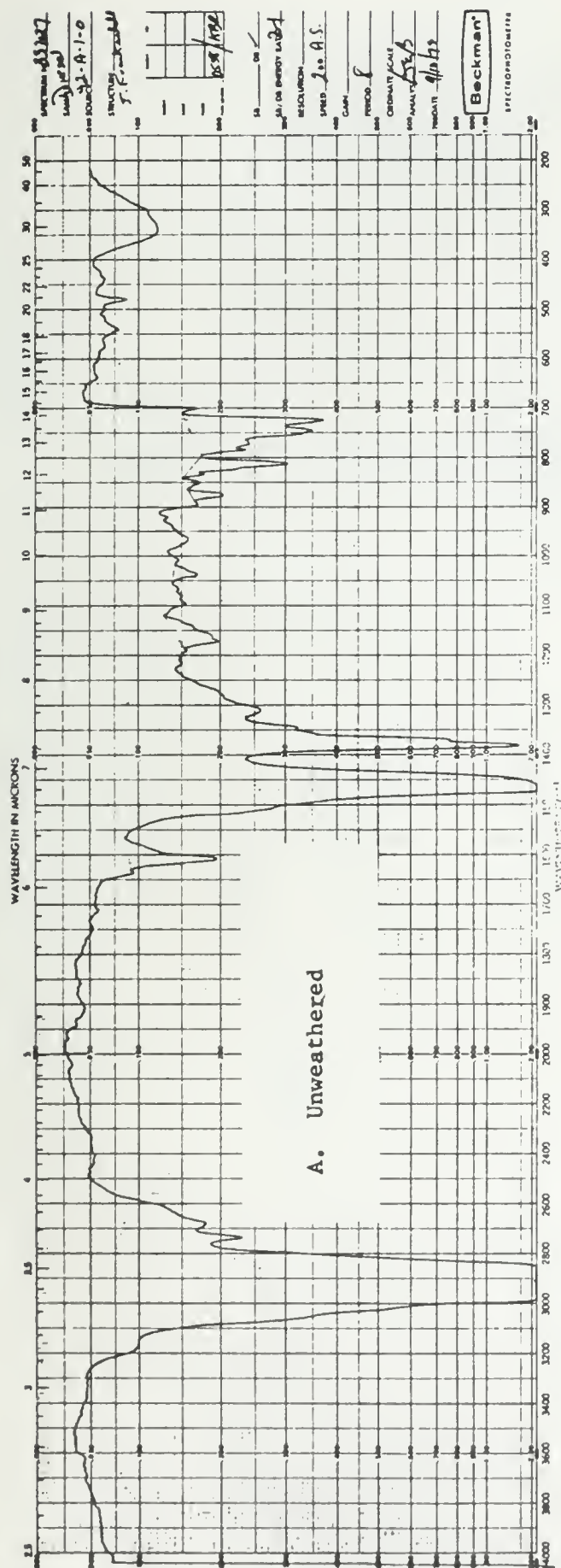


Figure 30. IR SPECTRUM OF UNWEATHERED PREMIUM GRADE GASOLINE 46-A-1-0

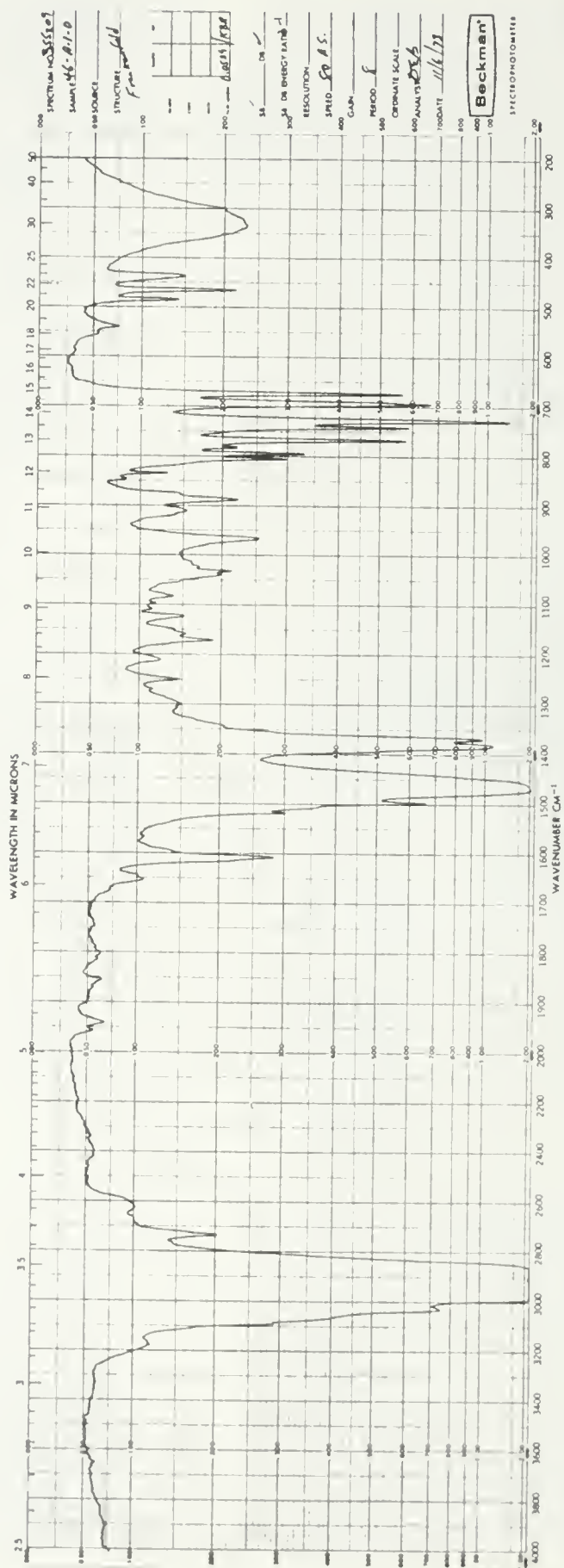


Figure 31. IR SPECTRA OF JET FUEL 43-A-1

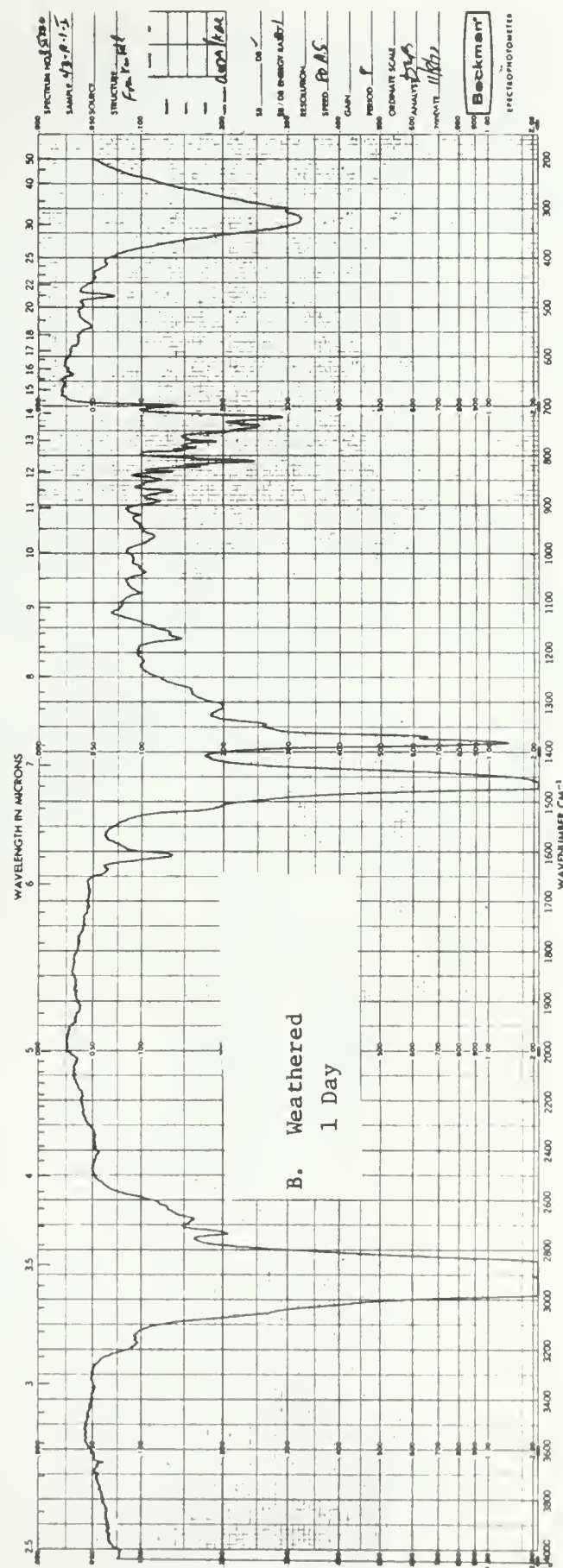
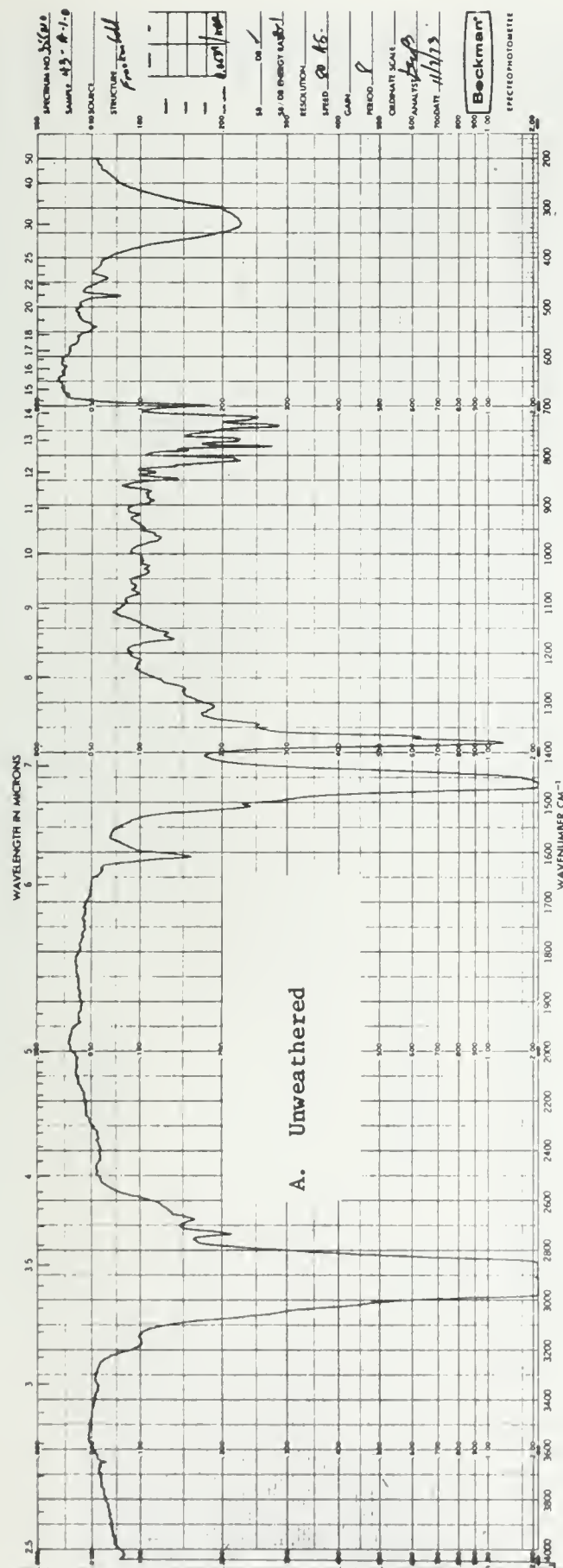


Figure 32. IR SPECTRA OF LUBE OIL 50-A-1

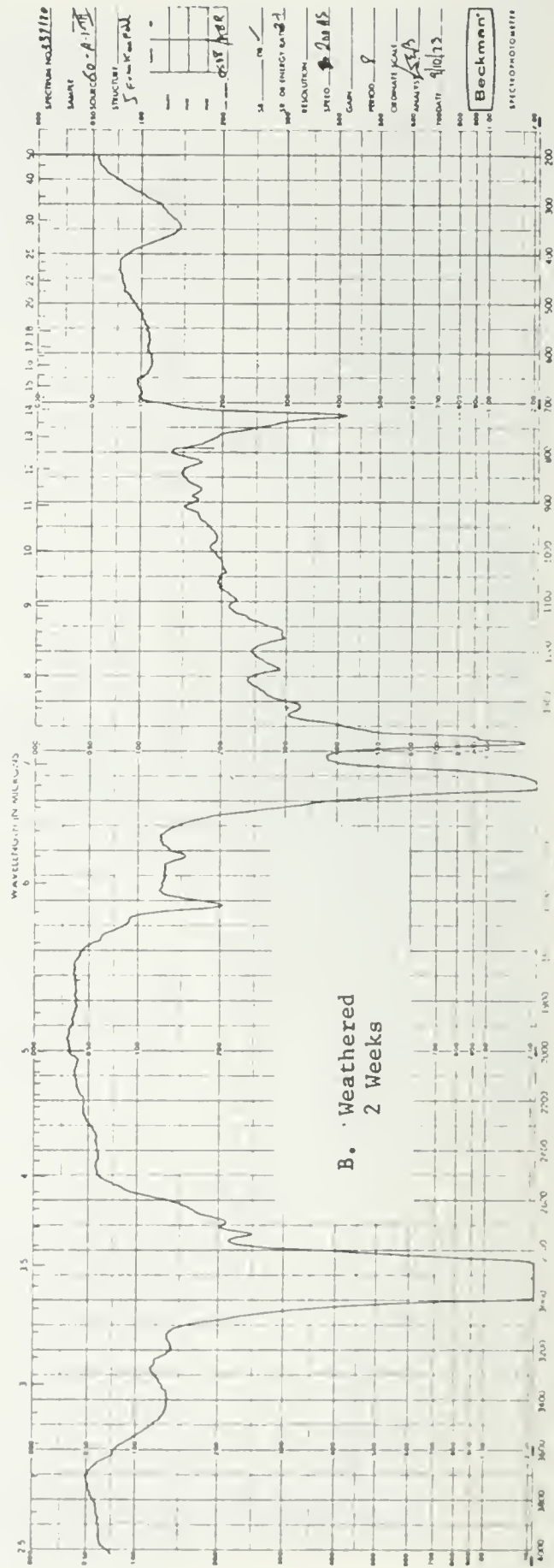
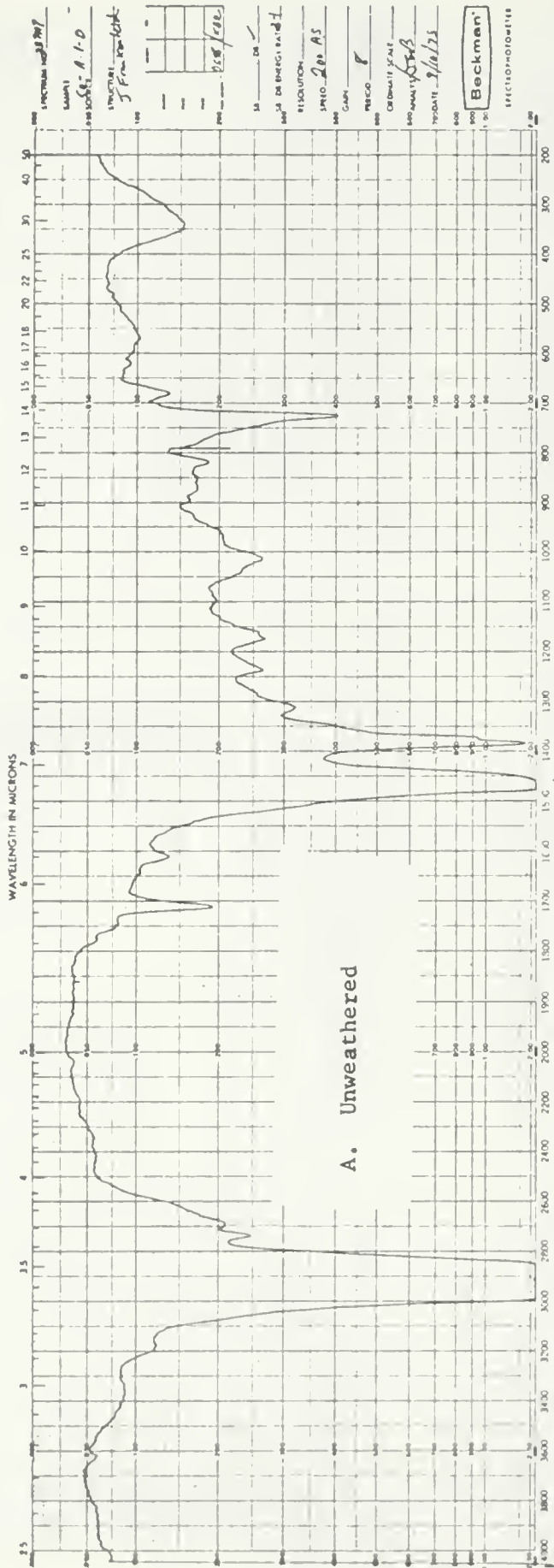
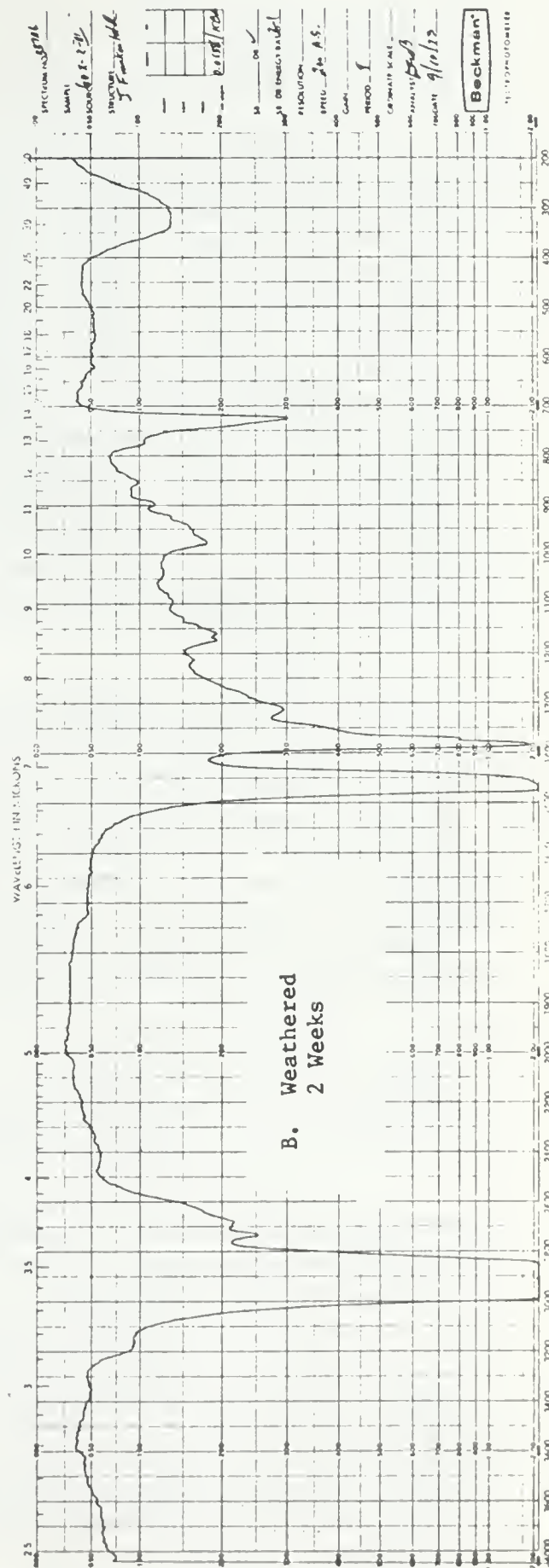
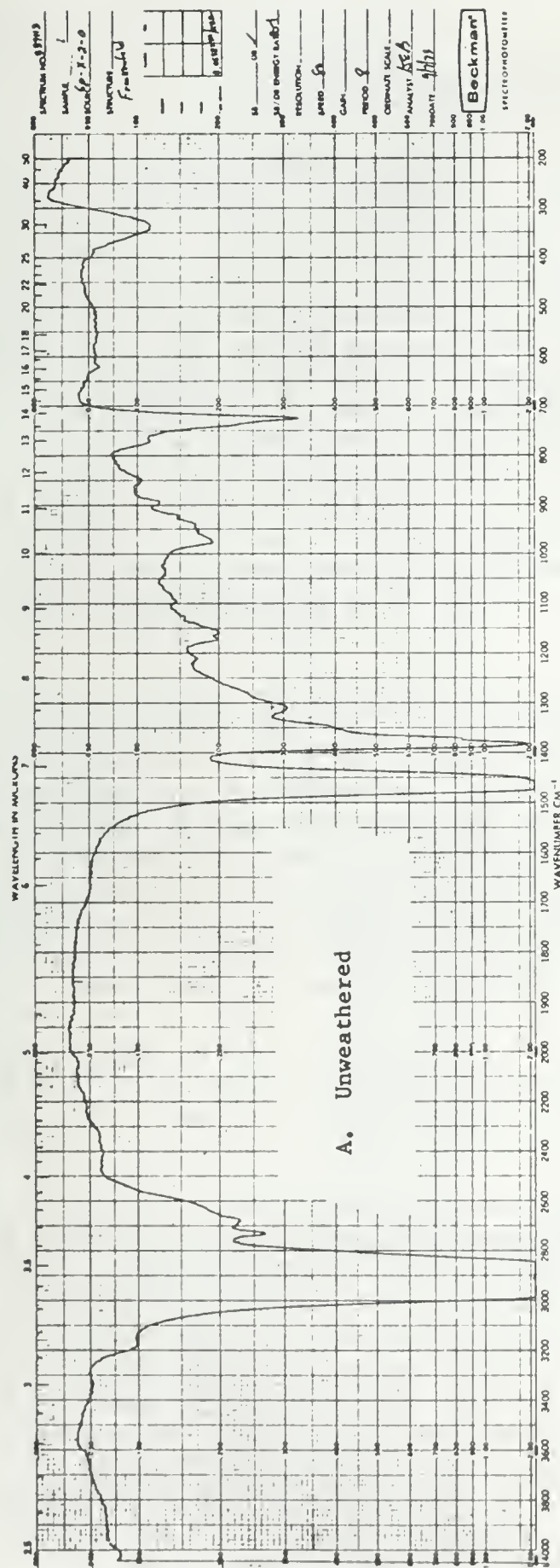


Figure 33. IR SPECTRA OF WHITE OIL 60-X-2



IV.5.4 Infrared as an Identification Technique

This would appear to be the major application of this technique. No two oils have identical spectra. As examples, spectra for two crude oils, which appear quite similar when fresh, are shown in Figures 34 and 35. These crudes, 10-A-14 and 10-B-1 originate in the U.S. and Persian Gulf respectively. After weathering, significant variations in the spectra appear, especially in the relative intensities of the bands at 725 cm^{-1} , 745 cm^{-1} , 810 cm^{-1} and 870 cm^{-1} . Differences in the $1000\text{ cm}^{-1} - 1200\text{ cm}^{-1}$ are also quite obvious. The patterns of bands in the fresh crudes appear very similar but again relative intensities of certain bands may be used for distinguishing between the two (31). Unweathered crude 10-A-14, for example, has much stronger absorbances due to benzene and monosubstituted benzenes (675 cm^{-1} and 695 cm^{-1}). Further, the aromatic absorbance at about 1600 cm^{-1} is significantly more intense in 10-A-14. Many other differences of this type can be identified on close examination. The spectra for these crudes are also quite distinct from those discussed above (Figures 25 and 26).

Spectra for two heating oils are given in Figures 36 and 37. These may also be compared with Figure 28. The oils 40-A-3 (Figure 37) and 40-A-1 (Figure 28) are different runs from the same refinery. The major discernable differences in these three oils lie in their degree of aromatic character; 40-A-1 the most and 40-A-2 the least. This is evidenced by very strong bands at 775 cm^{-1} , 810 cm^{-1} and 1600 cm^{-1} in 40-A-1. Another obvious difference, although somewhat less reliable as a fingerprint is the much larger peak at 1700 cm^{-1} , due to oxidation during weathering. This also correlates with a high aromatic and/or olefinic content (1). Another region showing variation is from $1150\text{ cm}^{-1} - 1200\text{ cm}^{-1}$.

Three different distillate fuels of the diesel type are shown in Figures 38-40. The spectra are quite different in the $700\text{ cm}^{-1} - 900\text{ cm}^{-1}$ region and with respect to degree of aromaticity as shown by the relative strengths of the 1600 cm^{-1} bands.

A quite different picture is presented by the spectra of lube oils (Figures 32 and 41-42). Here the most important regions are $1100\text{ cm}^{-1} - 1350\text{ cm}^{-1}$ and around 1700 cm^{-1} where the more persistent characteristic additives appear. Bands due to additives are also seen at 675 cm^{-1} and 1010 cm^{-1} in the unweathered lubes (Figures 32A, 41A and 42A). These, however, are soluble and largely disappear on weathering over salt water. More and larger amounts of additives are shown in the premium lube oils (Figures 32 and 42) as compared to less expensive oils (Figure 41). Also noteworthy are the different types of additives used in the various lubes. Thus, the spectra of 50-D-2 has strong bands at 1735 cm^{-1} and 1160 cm^{-1} (Figure 43) absent in both 50-A-1 and 50-D-1. The spectra of 50-A-1 has strong absorbance at 1710 cm^{-1} , not present in either of the others (but common to many lubes). As pointed out above, an additive present in many lubes including all three in Figures 41-43, but absent in other oils, appears at 1235 cm^{-1} .

FIGURE 34. IR SPECTRA OF CRUDE 10-A-14

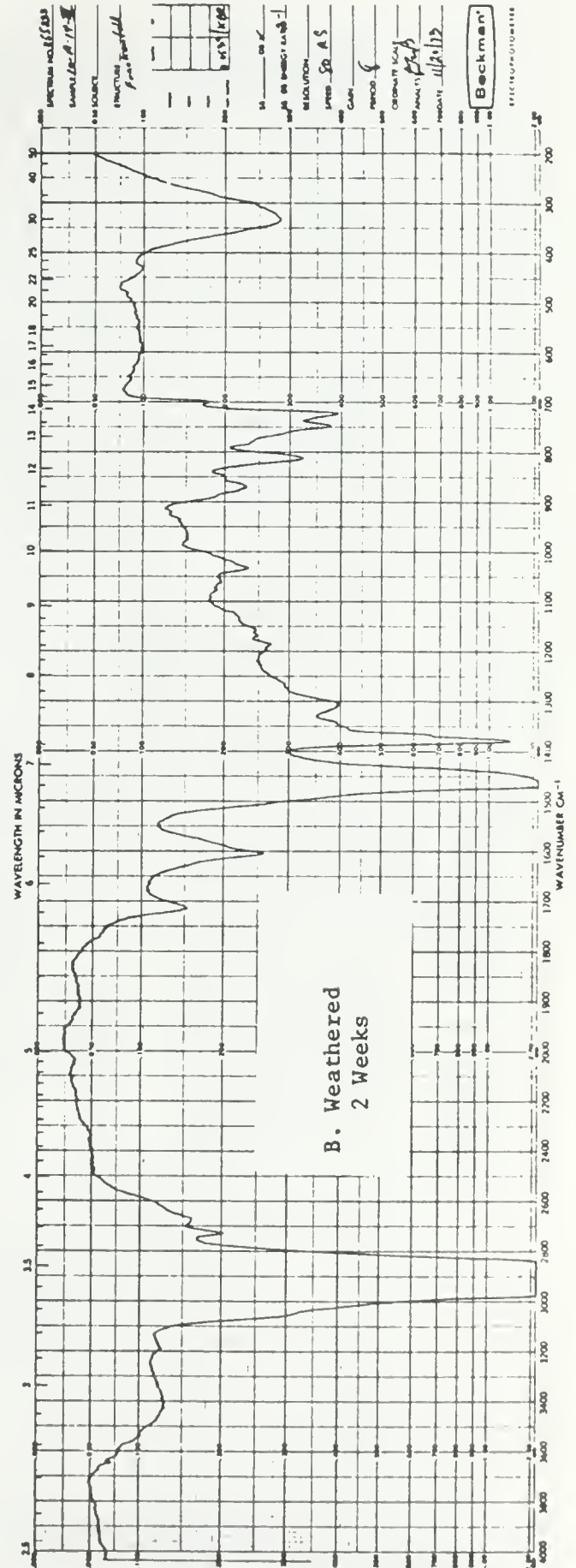
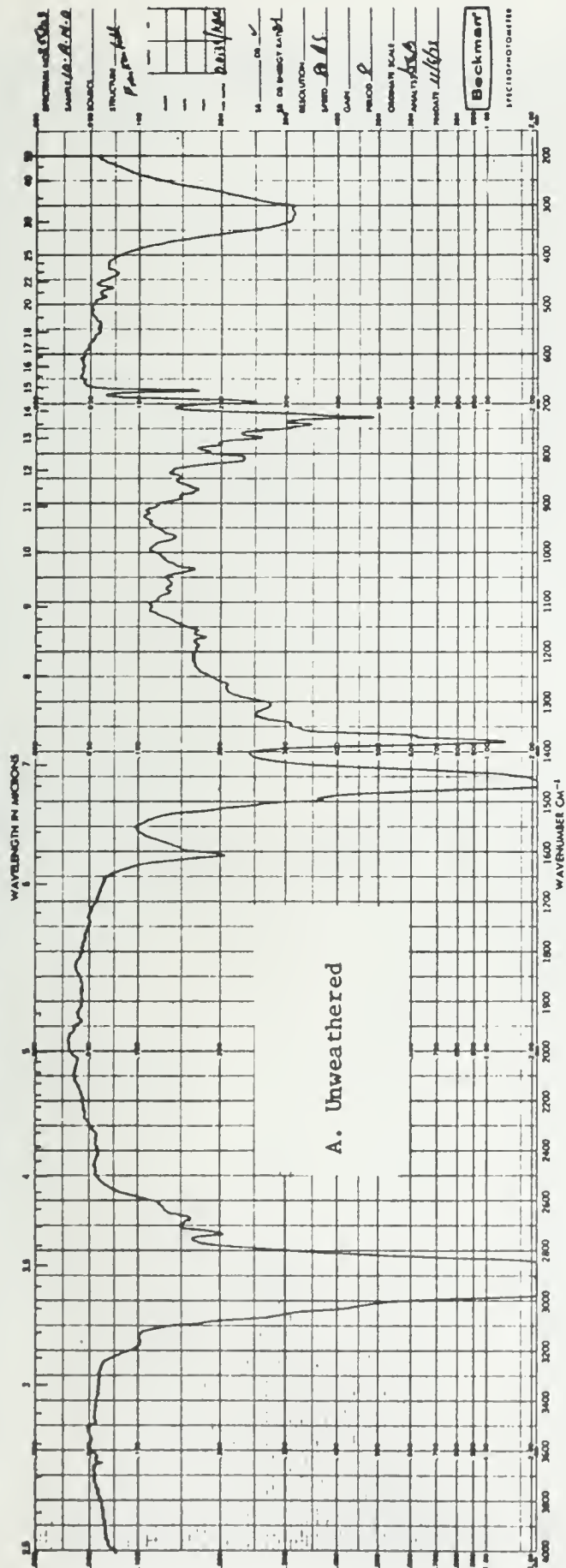


FIGURE 35. IR SPECTRA OF CRUDE 10-B-1

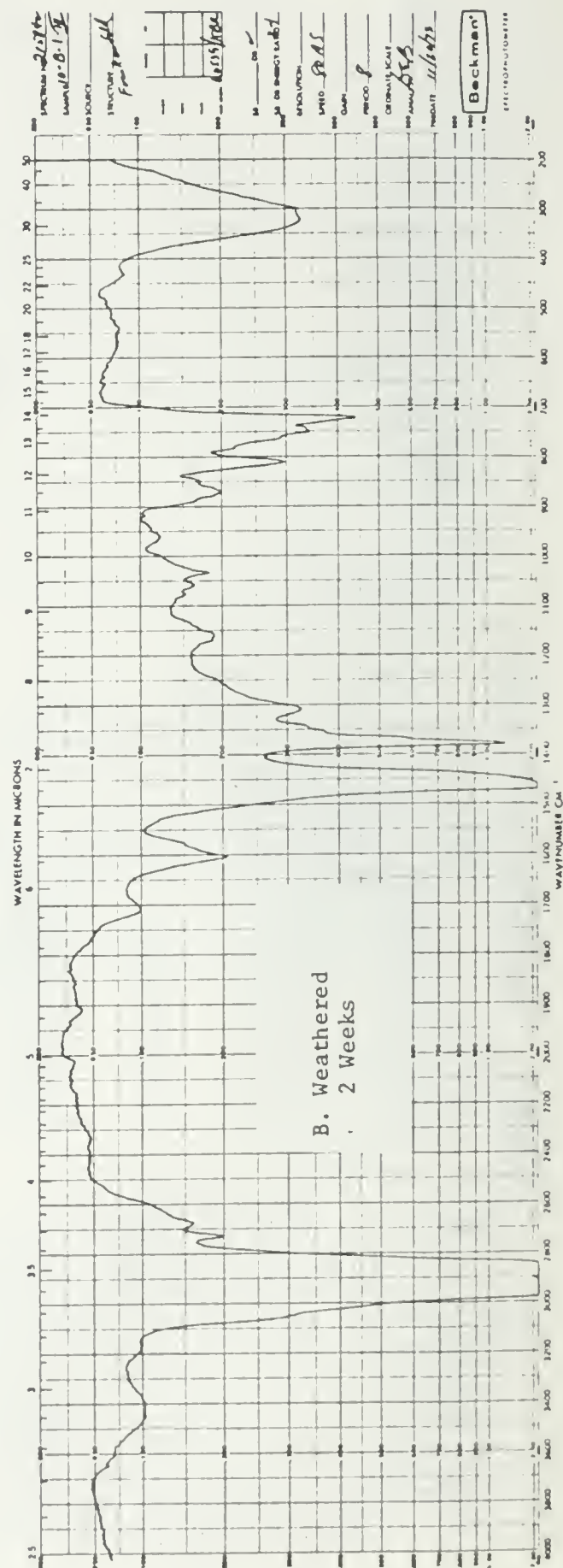
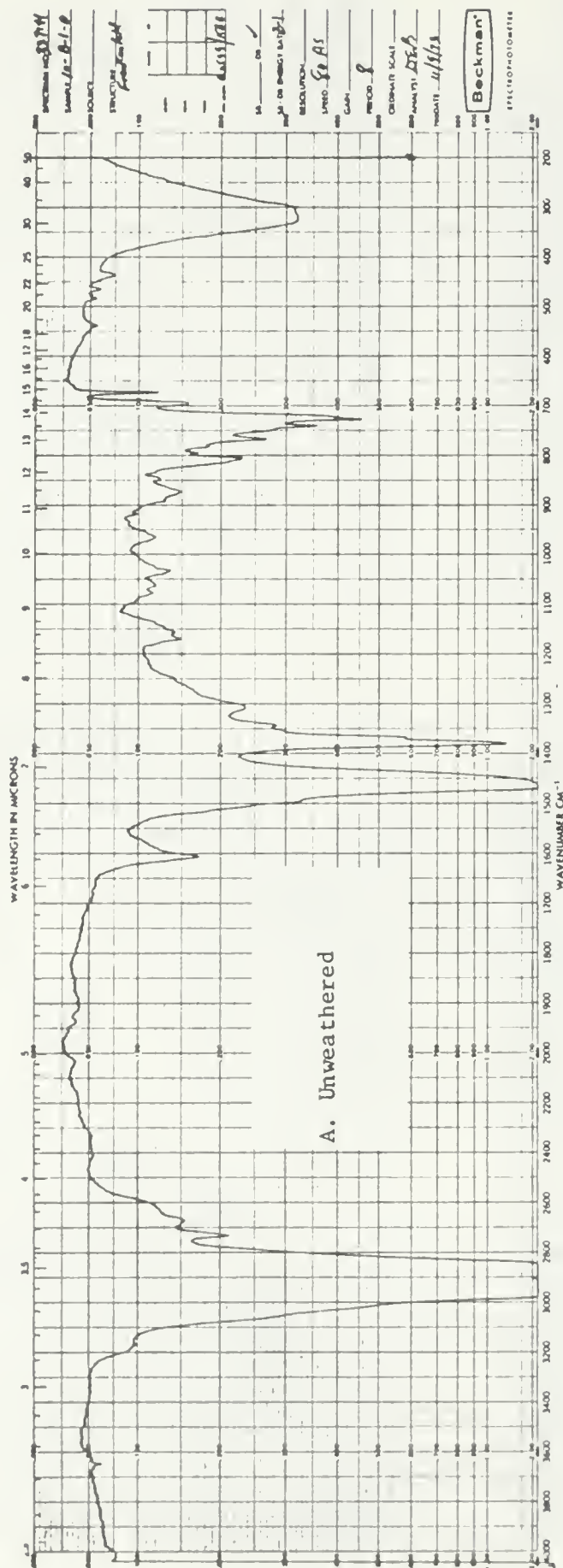


FIGURE 37. IR SPECTRA OF NO. 2 HEATING OIL 40-A-3-0

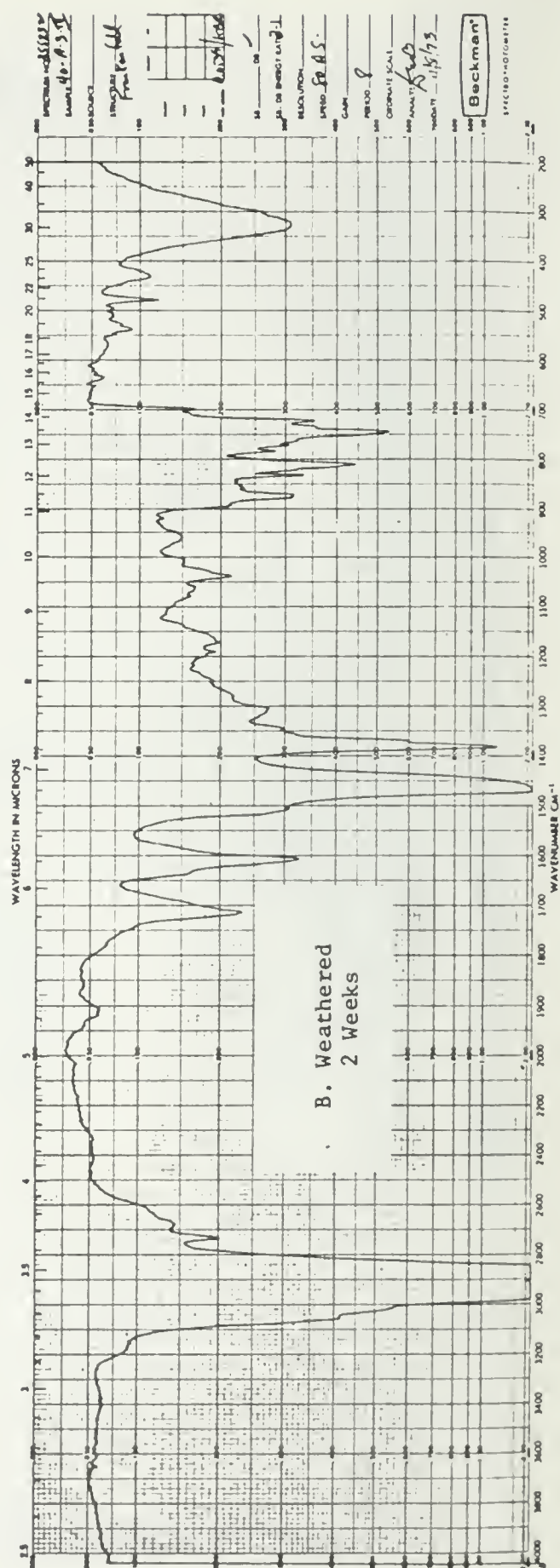
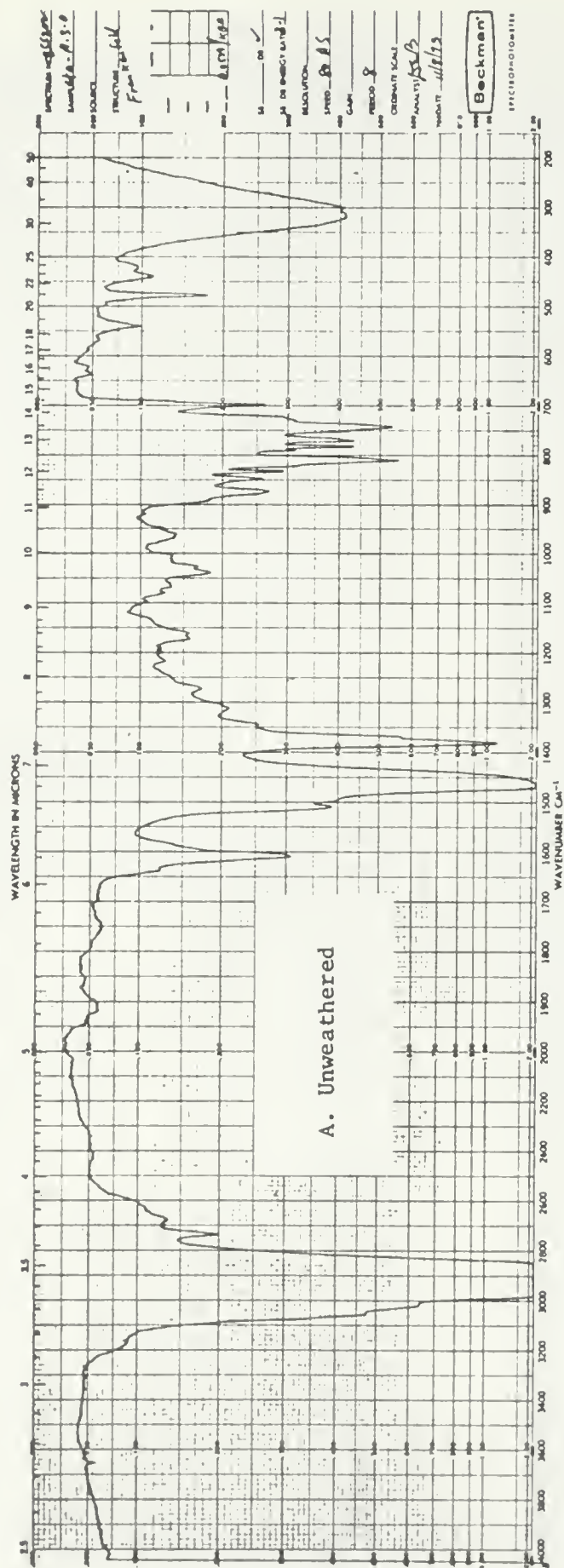


FIGURE 38.

IR SPECTRA OF AUTOMOTIVE DIESEL 42-A-1

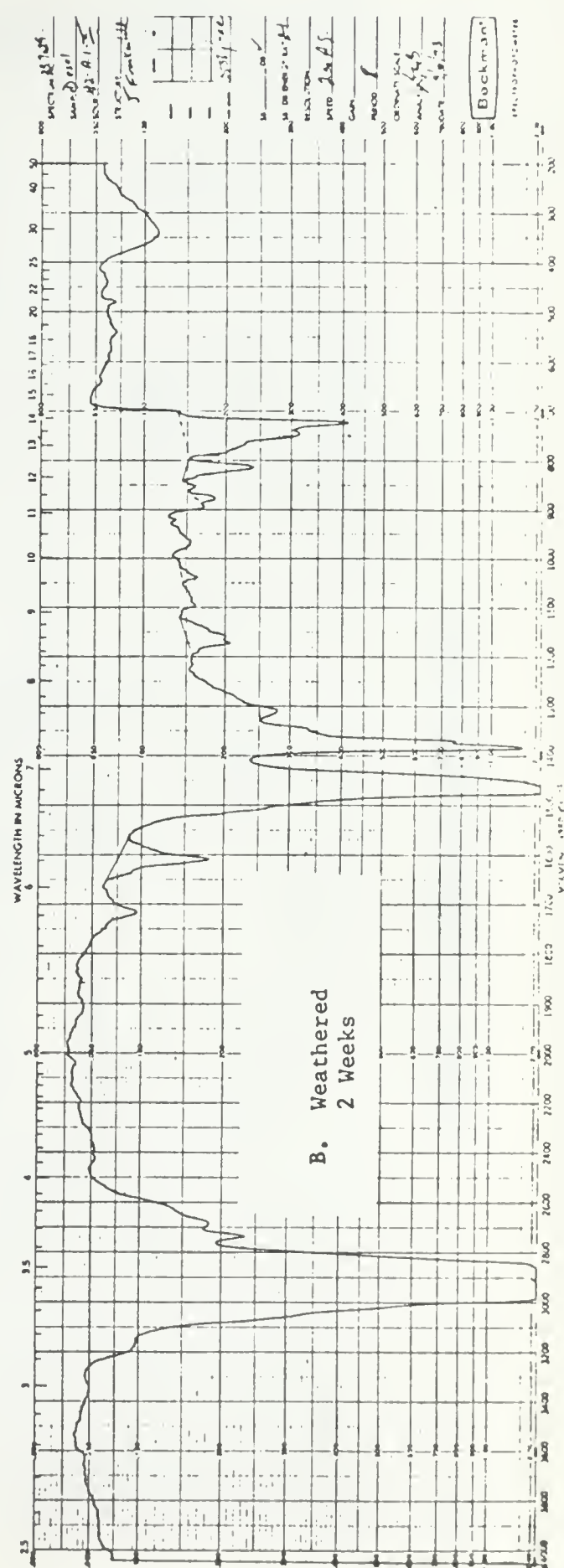
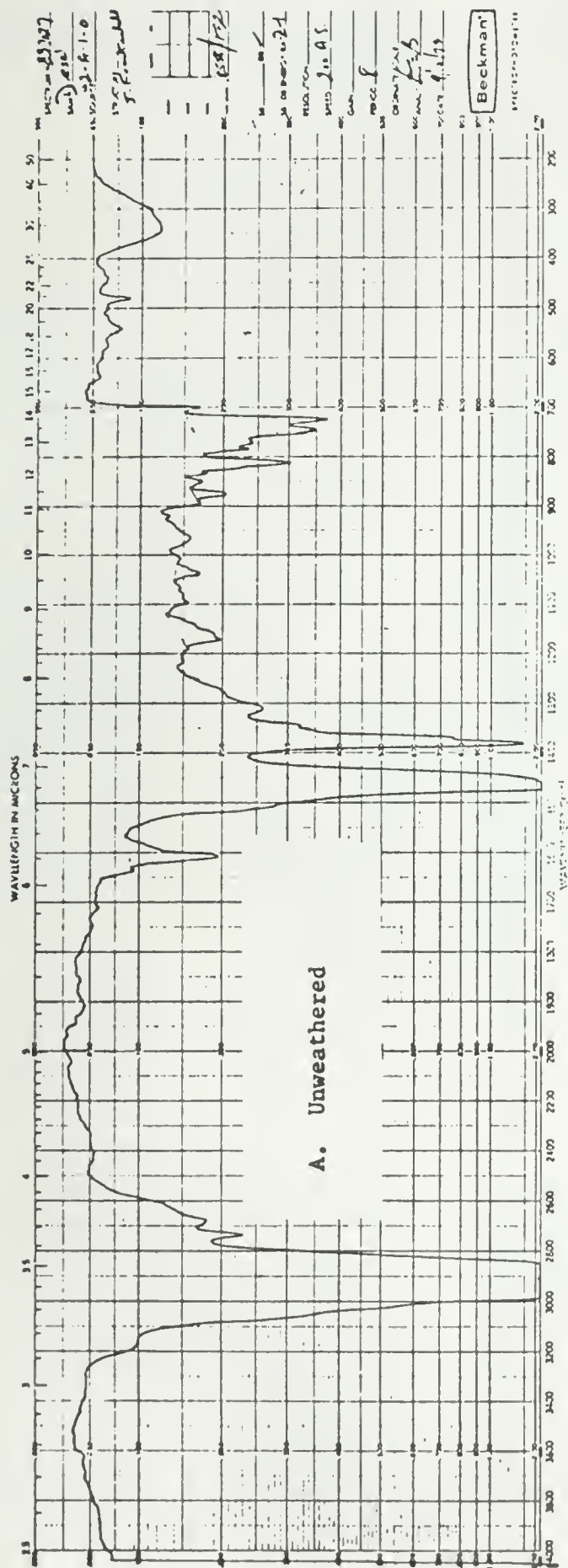


FIGURE 39. IR SPECTRA OF DIESEL 42-A-2

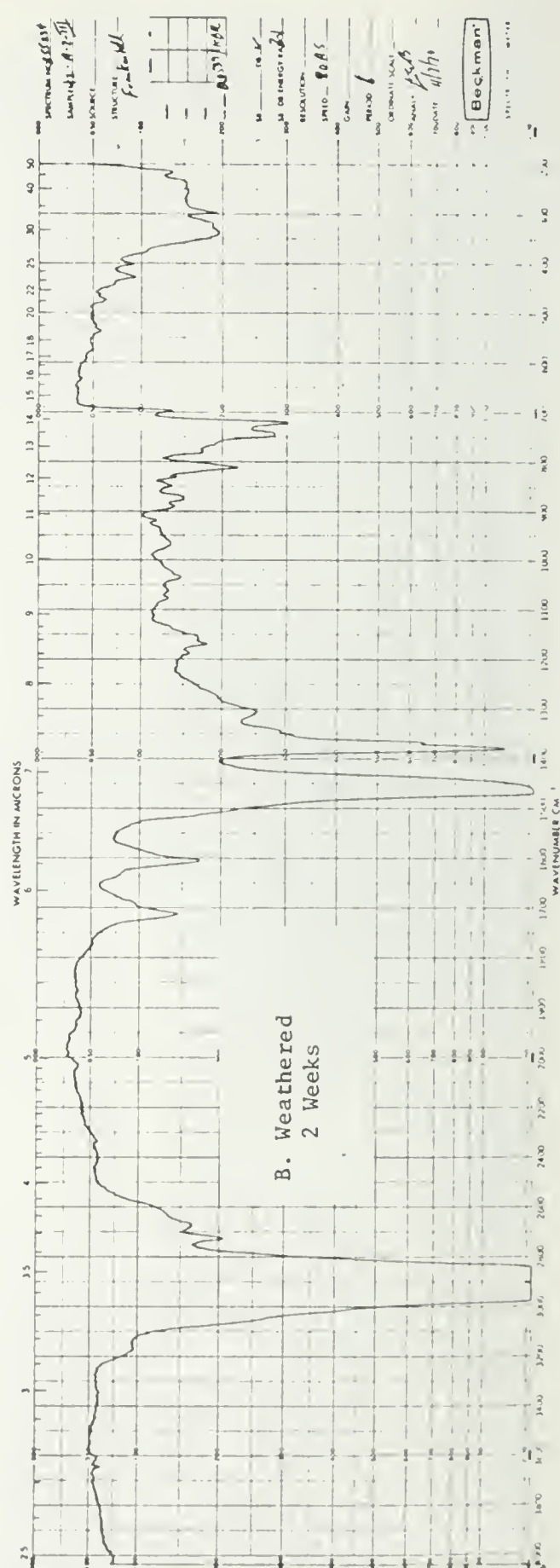
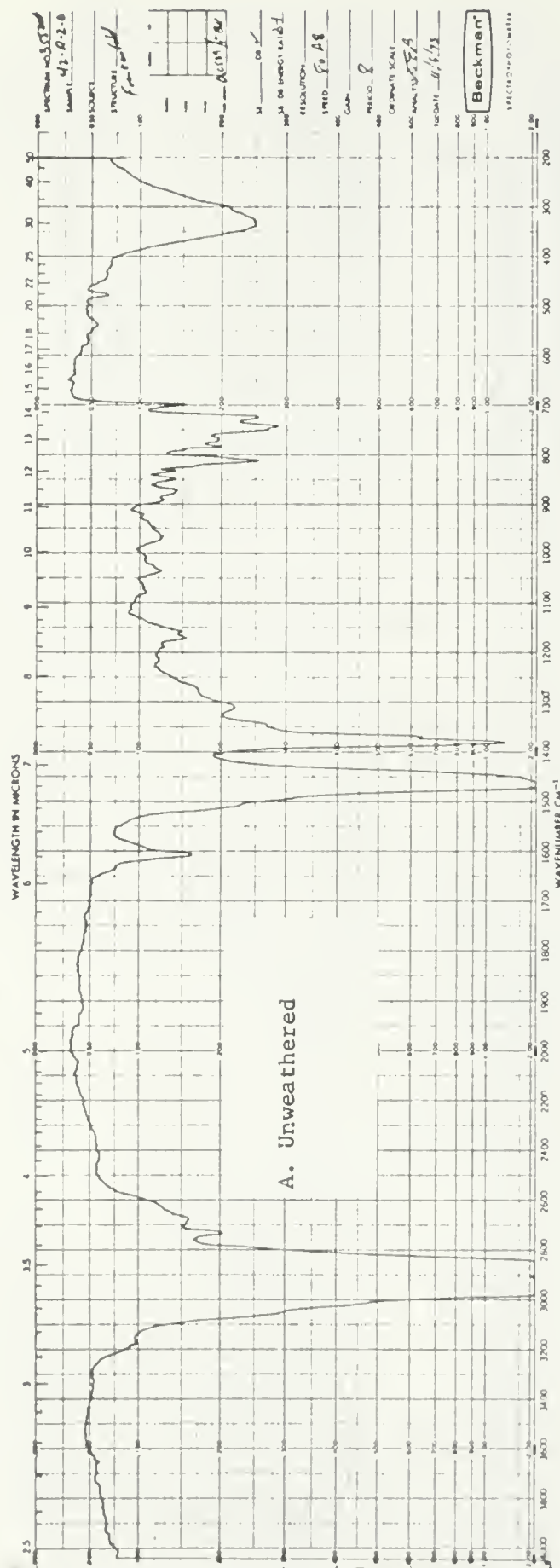


FIGURE 40. IR SPECTRA OF DIESEL 42-A-3

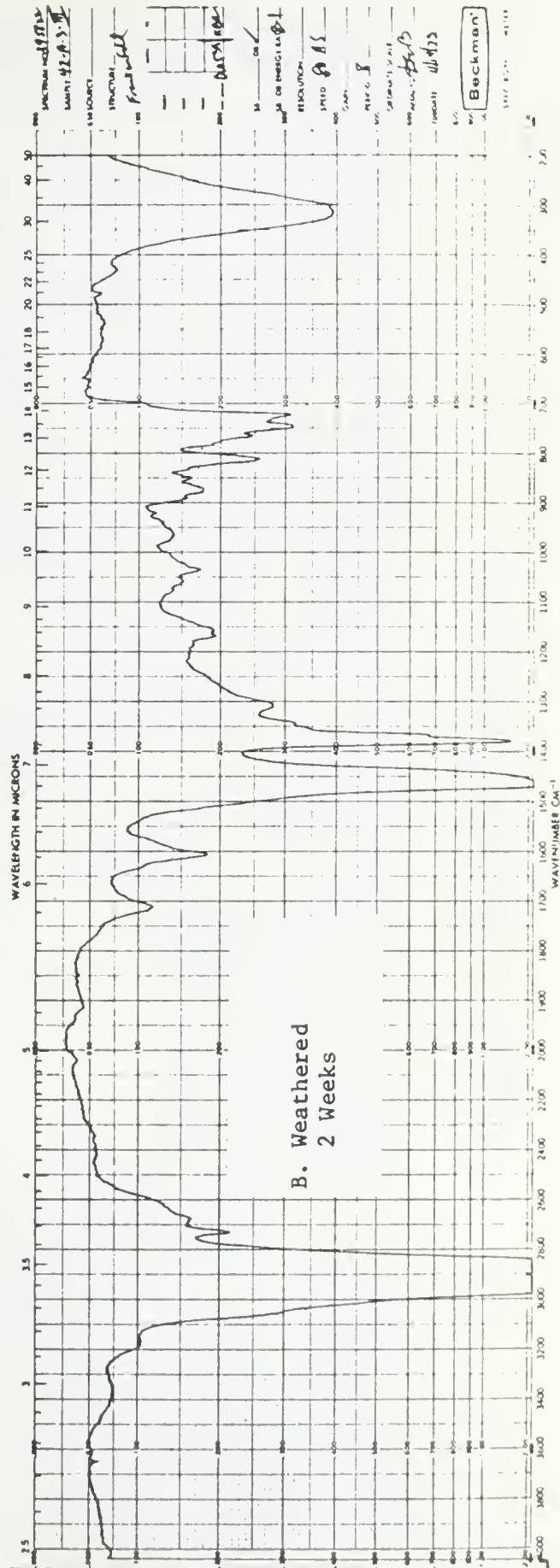
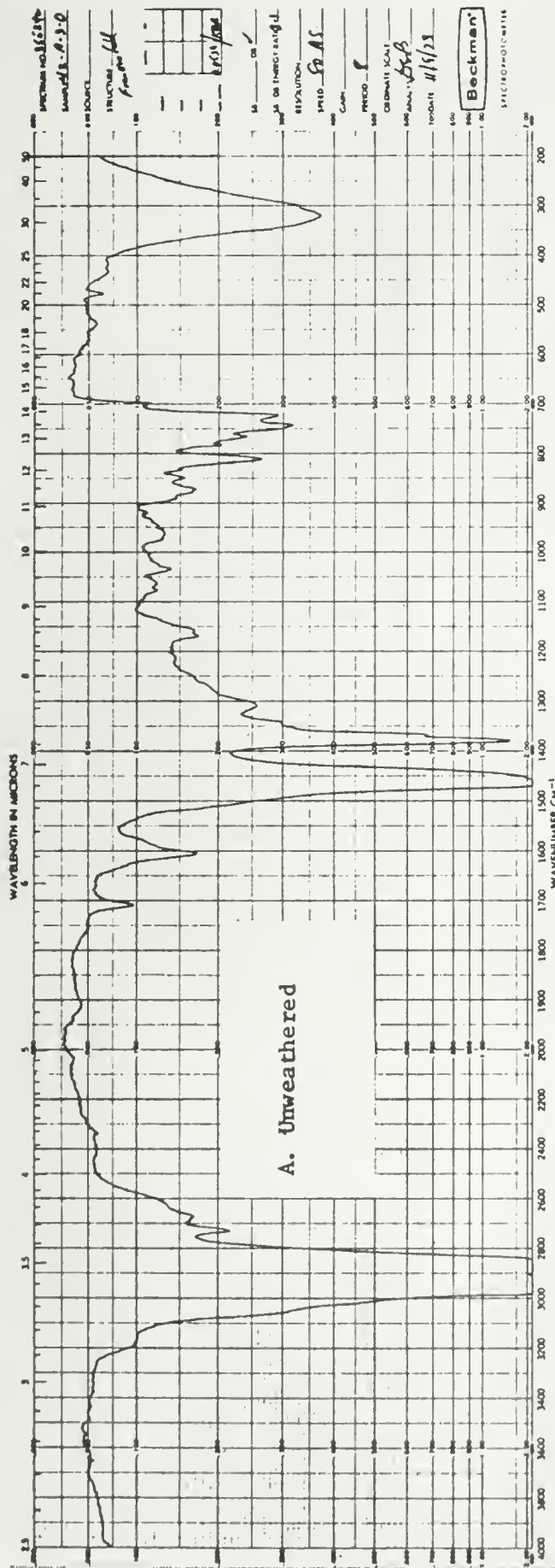


FIGURE 41. IR SPECTRA OF LUBE OIL 50-D-1

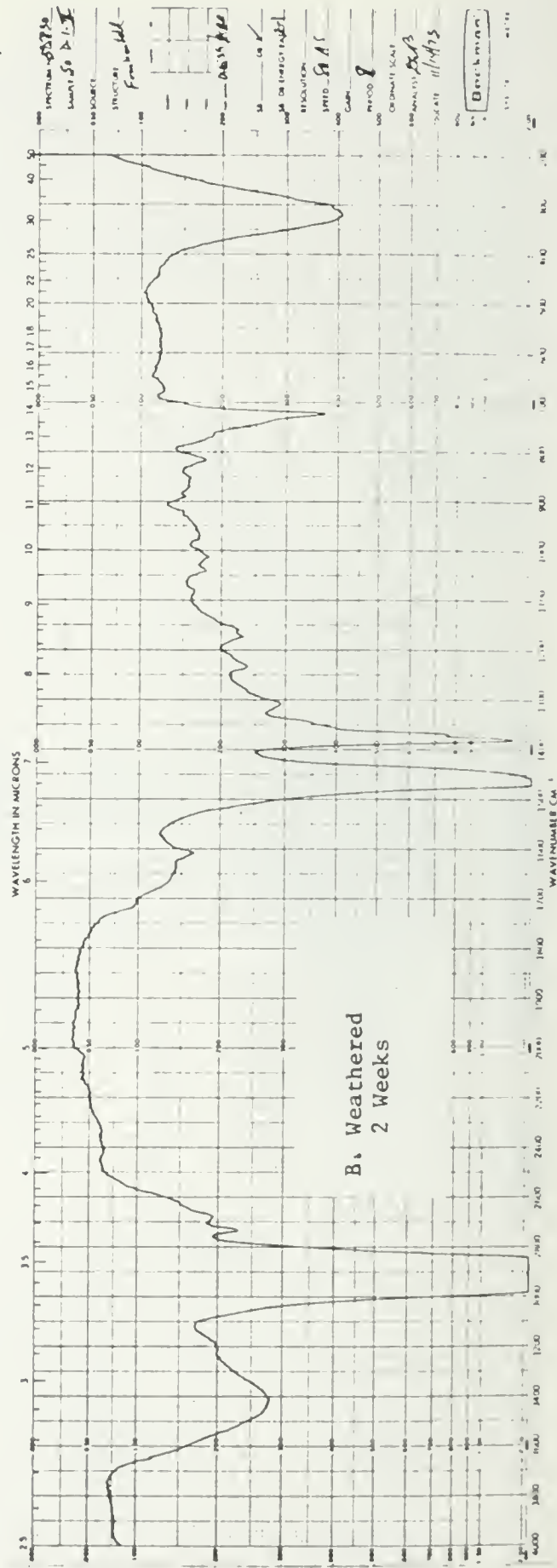
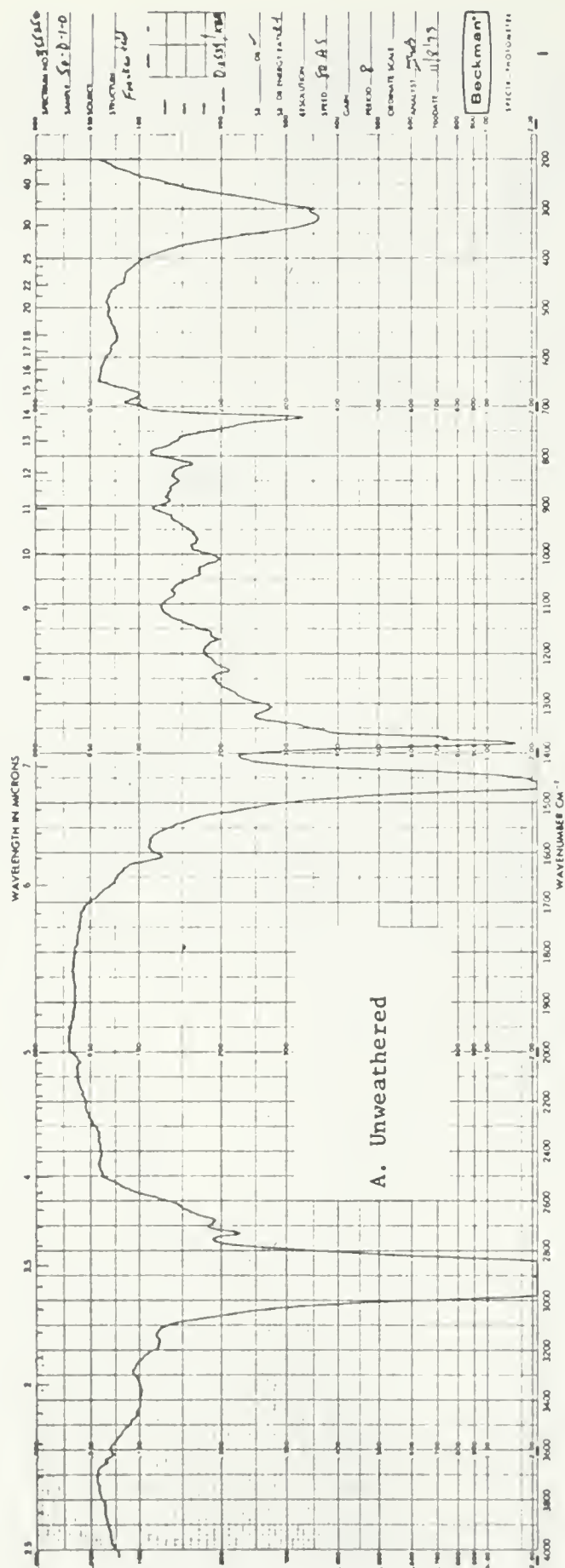


FIGURE 42.
IR SPECTRA OF LUBE OIL 50-D-2

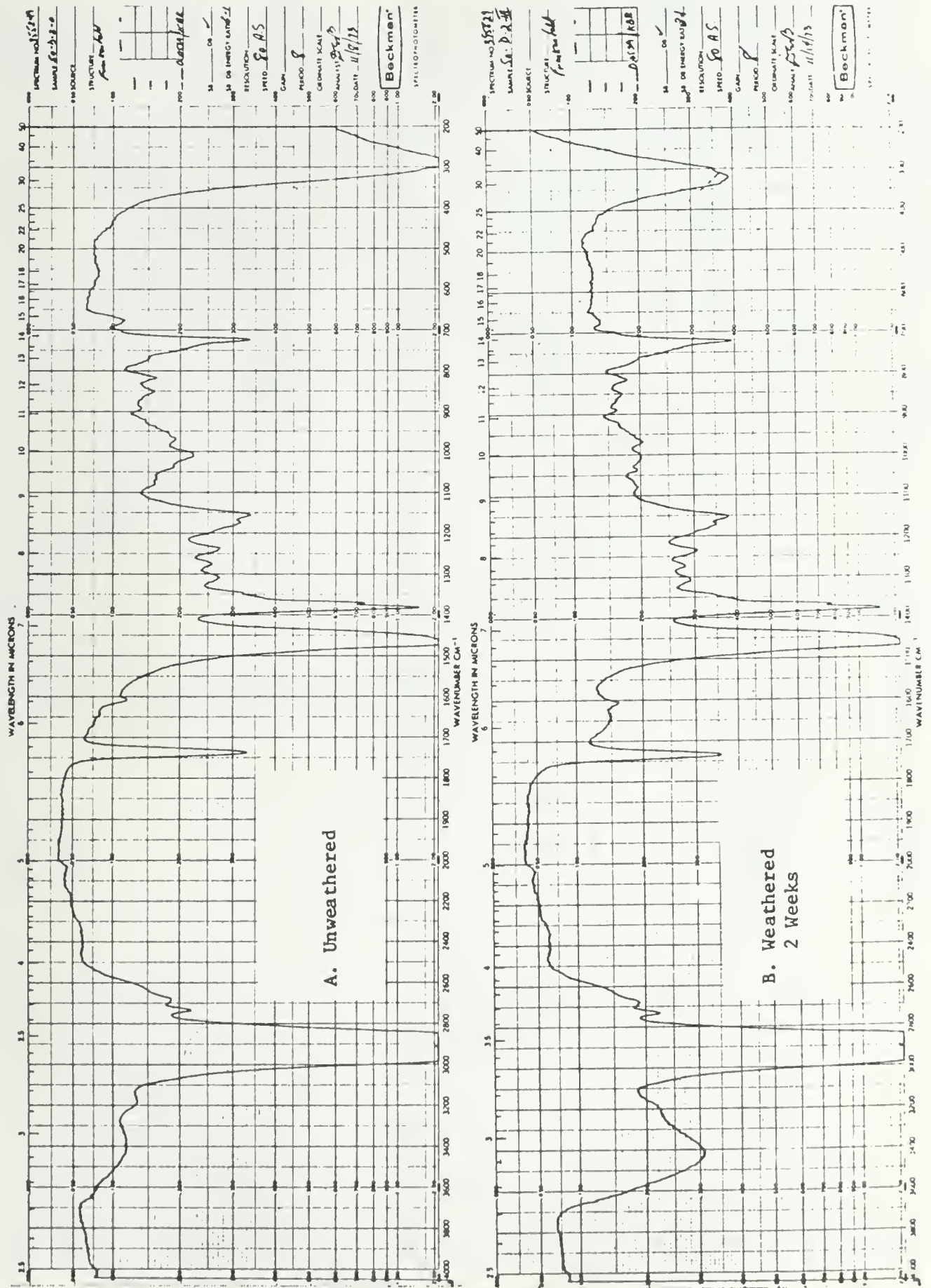


FIGURE 43. IR SPECTRA OF NO. 5 OIL 31-F-1

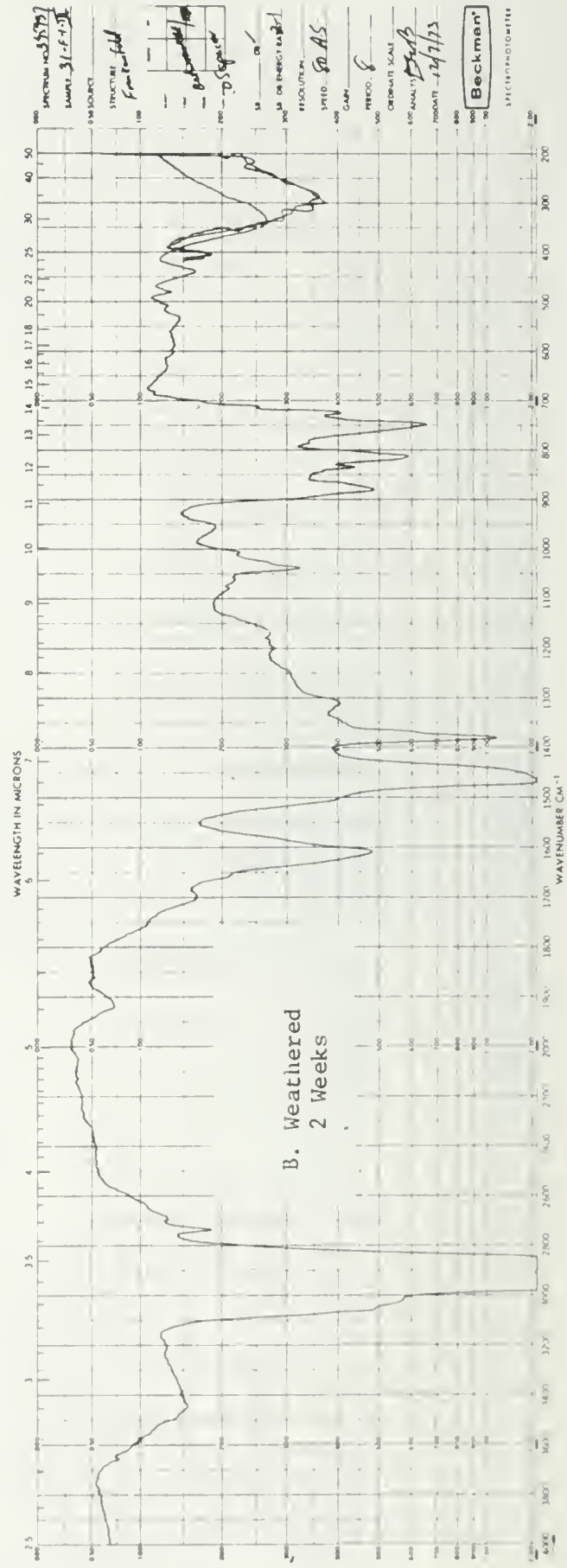
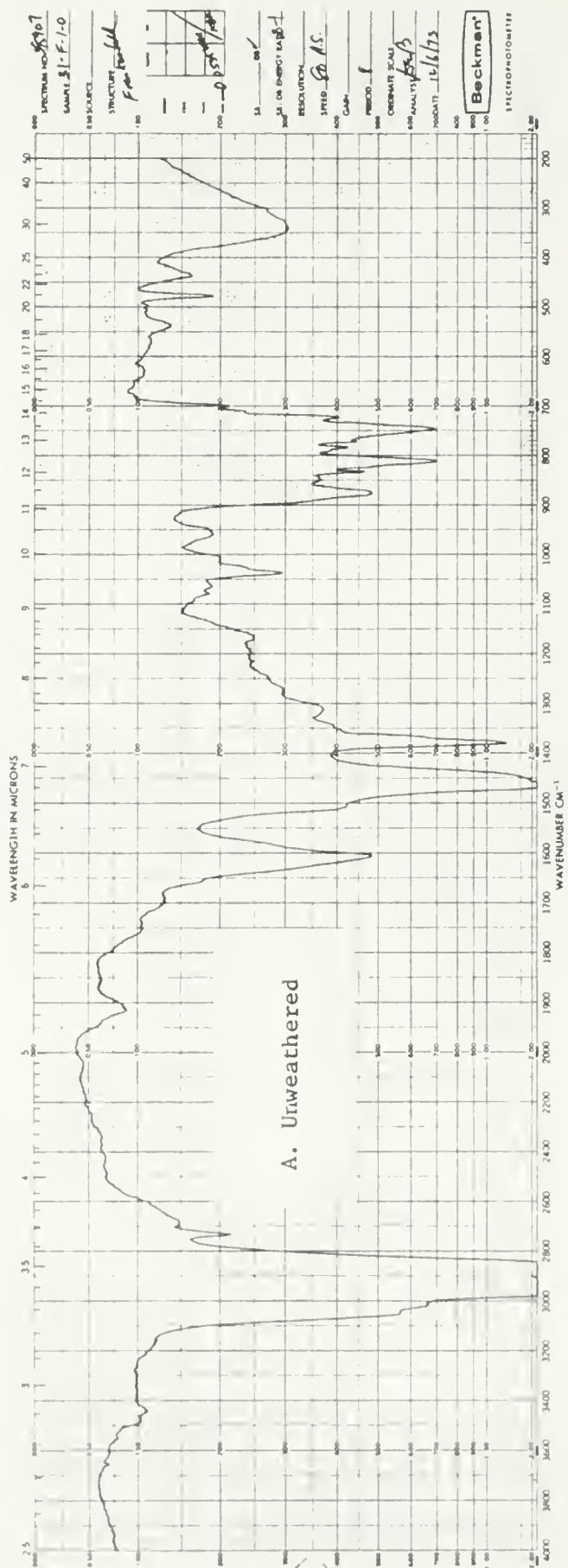


FIGURE 44. IR SPECTRA OF NO. 6 OIL 32-F-2

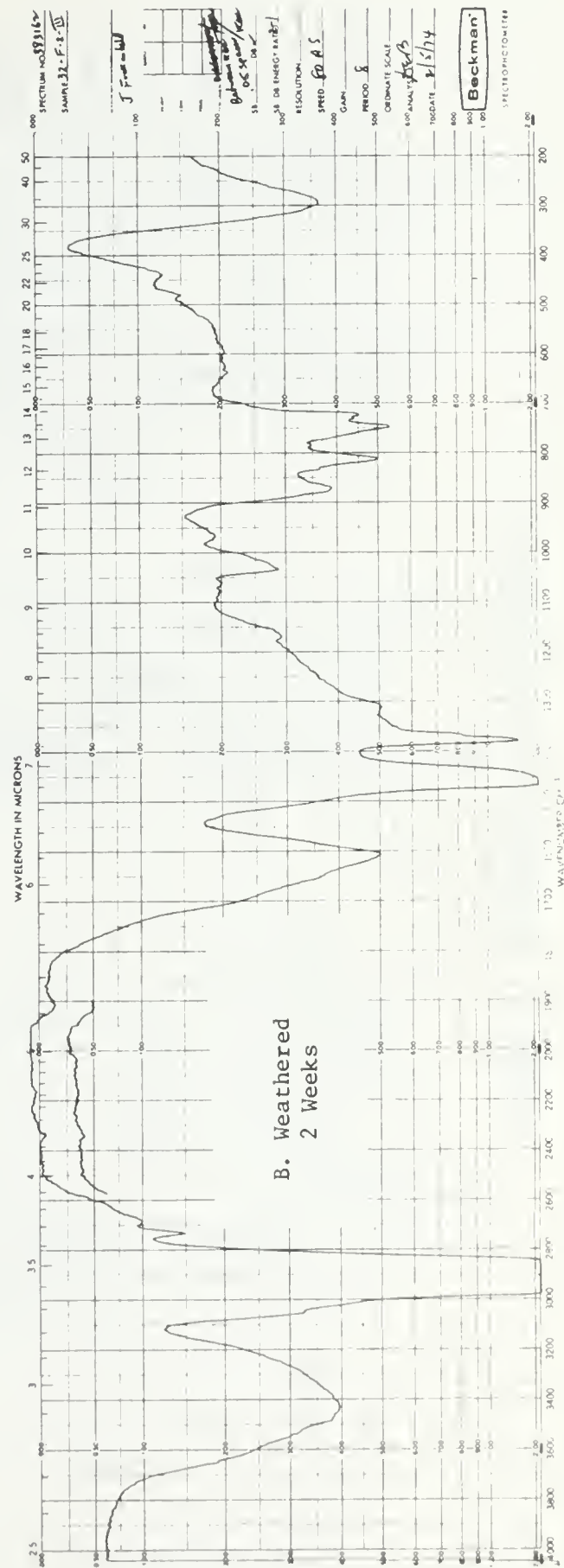
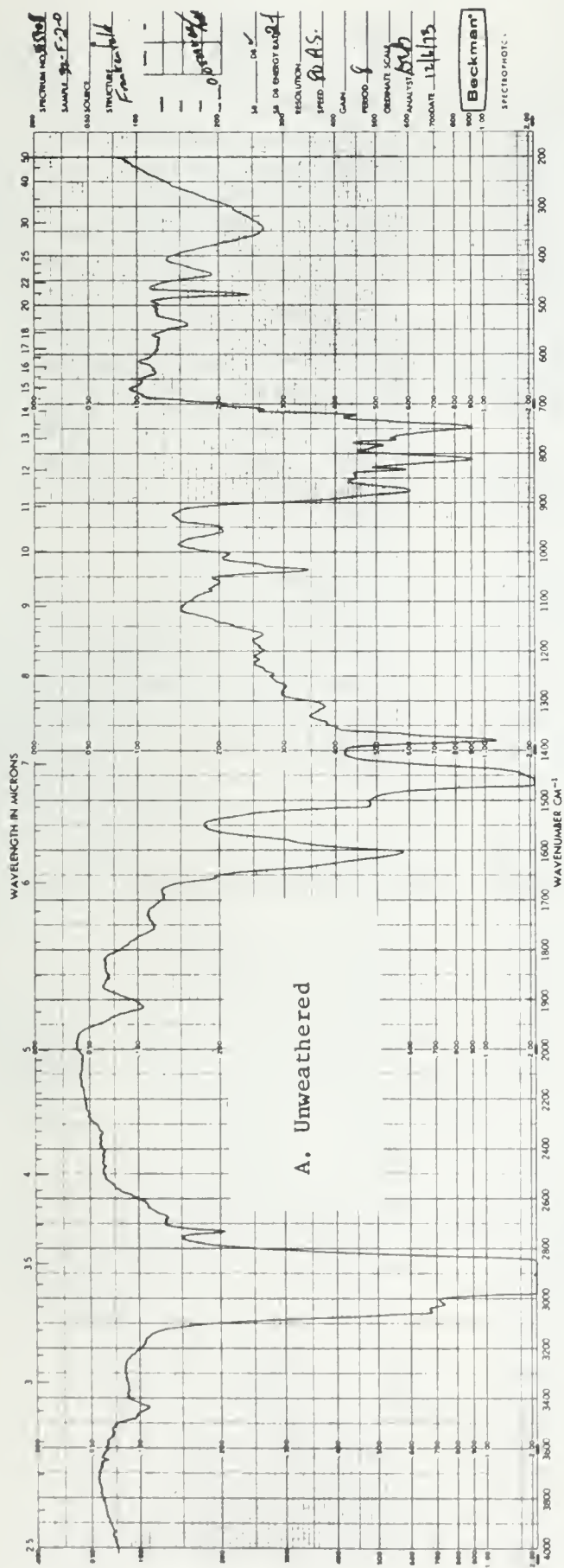
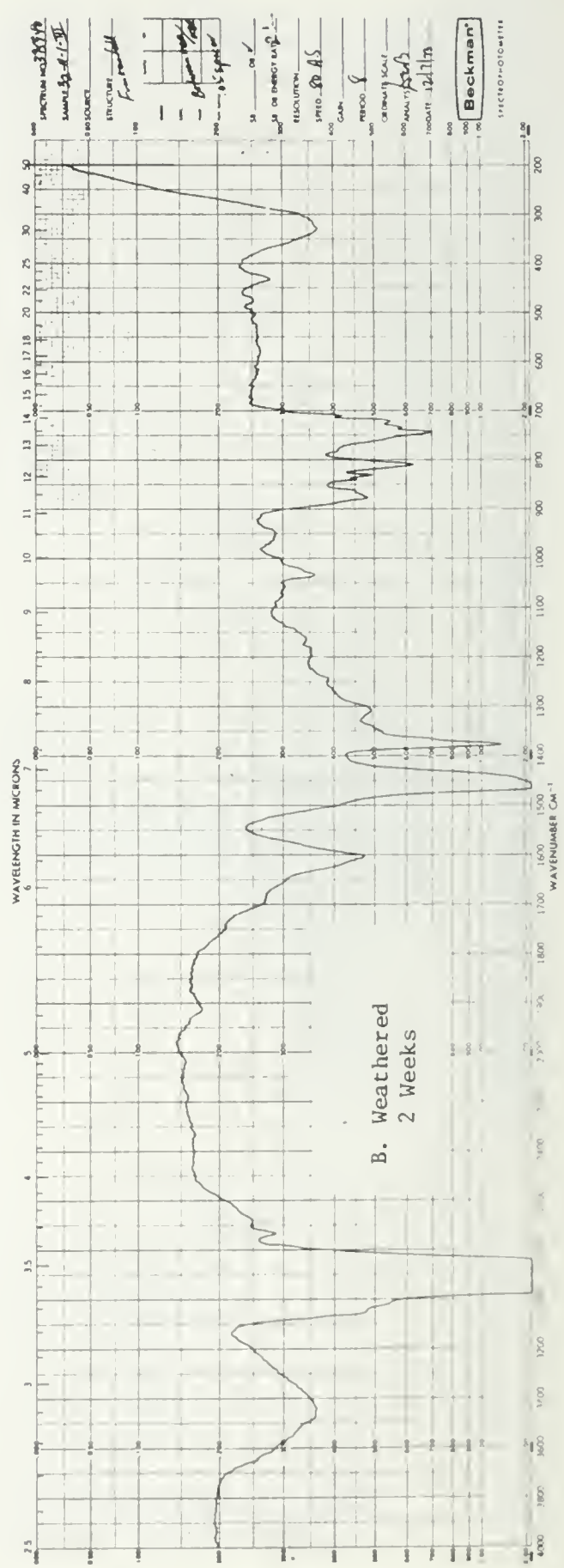
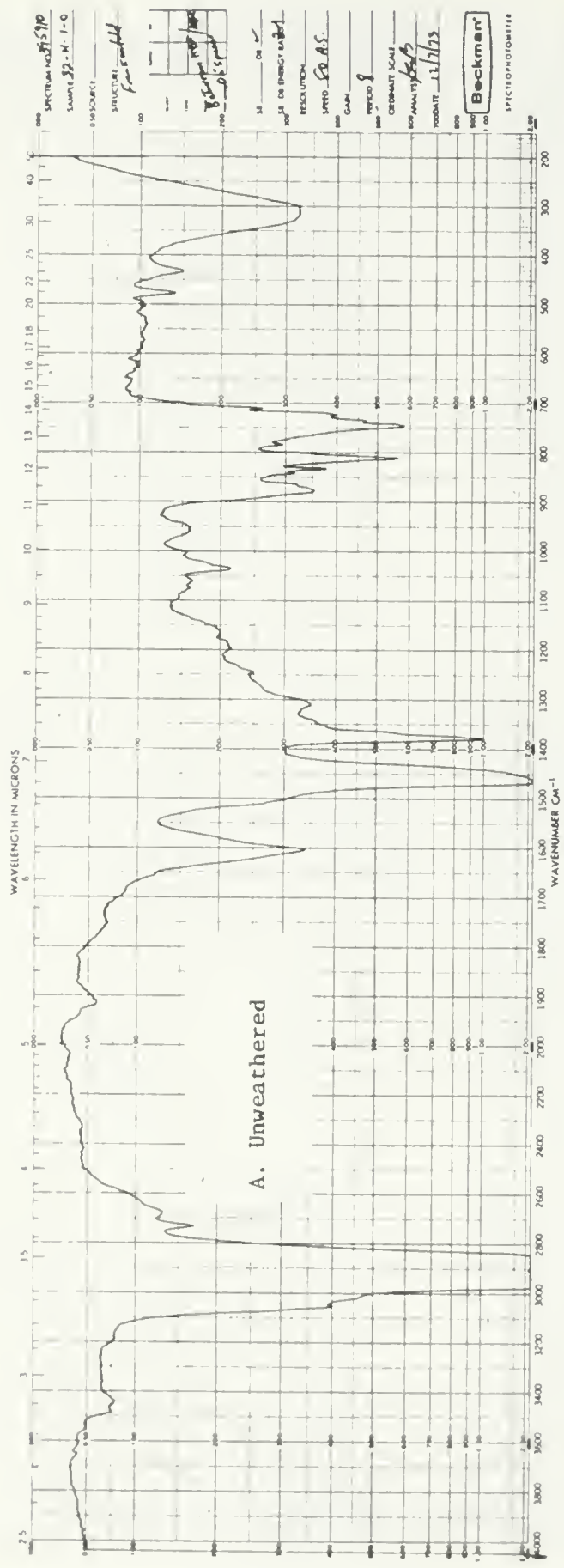


FIGURE 45. IR SPECTRA OF NO. 6 OIL 32-H-1



Spectra for three blended residual fuels are given in Figures 43-45. All three have similar characteristics making them difficult to classify (see previous subsection). However, there are significant differences in relative intensities in the 700-900 cm^{-1} region to permit unequivocal identification provided an authentic sample is available. It is noteworthy that weathering effects on these spectra are minimal.

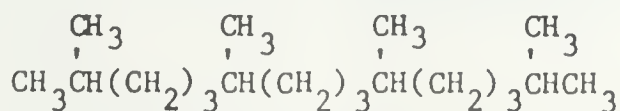
From the foregoing discussion, the usefulness of infrared spectroscopy as a fingerprinting tool is well established. When employed in conjunction with other analytical methods (Section V) it is one of the most powerful tools presently available.

IV.5.5 Use of Ratios of IR Absorbances In Fingerprinting

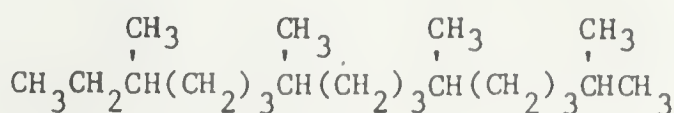
The foregoing discussions were purely qualitative. One can also treat IR data in a more quantitative manner by computing and comparing the ratios of absorbances of certain selected bands (13,21,26). We examined this technique, measuring the absorbances by hand. However, the errors were too great for precise results. Qualitative examination of spectra was both easier and more reliable. More sophisticated techniques, employing computer analysis, are being developed by others (26,31) and may serve to obviate this difficulty.

IV.6 Fingerprinting With Gas Chromatography

As pointed out in previous sections, one can obtain highly resolved gas chromatograms by going to longer columns of smaller diameter than those used in GC distillations. This improved resolution is quite apparent by comparing the GC fingerprint of crude oil 10-A-3 (Figure 46) with the corresponding GC distillation trace (Figure 16, Subsection IV.3). Noteworthy is the resolution of peaks at 17.5 and 18.8 min. retention time into well defined doublets (Figure 46). These have been identified (28, 29,32) as the isoprenoids pristane (A) and phytane (B) and the corresponding normal paraffins heptadecane ($n\text{-C}_{17}$) and octadecane ($n\text{-C}_{18}$). They are not identifiable in GC distillation traces. These peaks are excellent benchmarks both in qualitative interpretation of chromatograms and as quantitative indices (29,32).



A Pristane



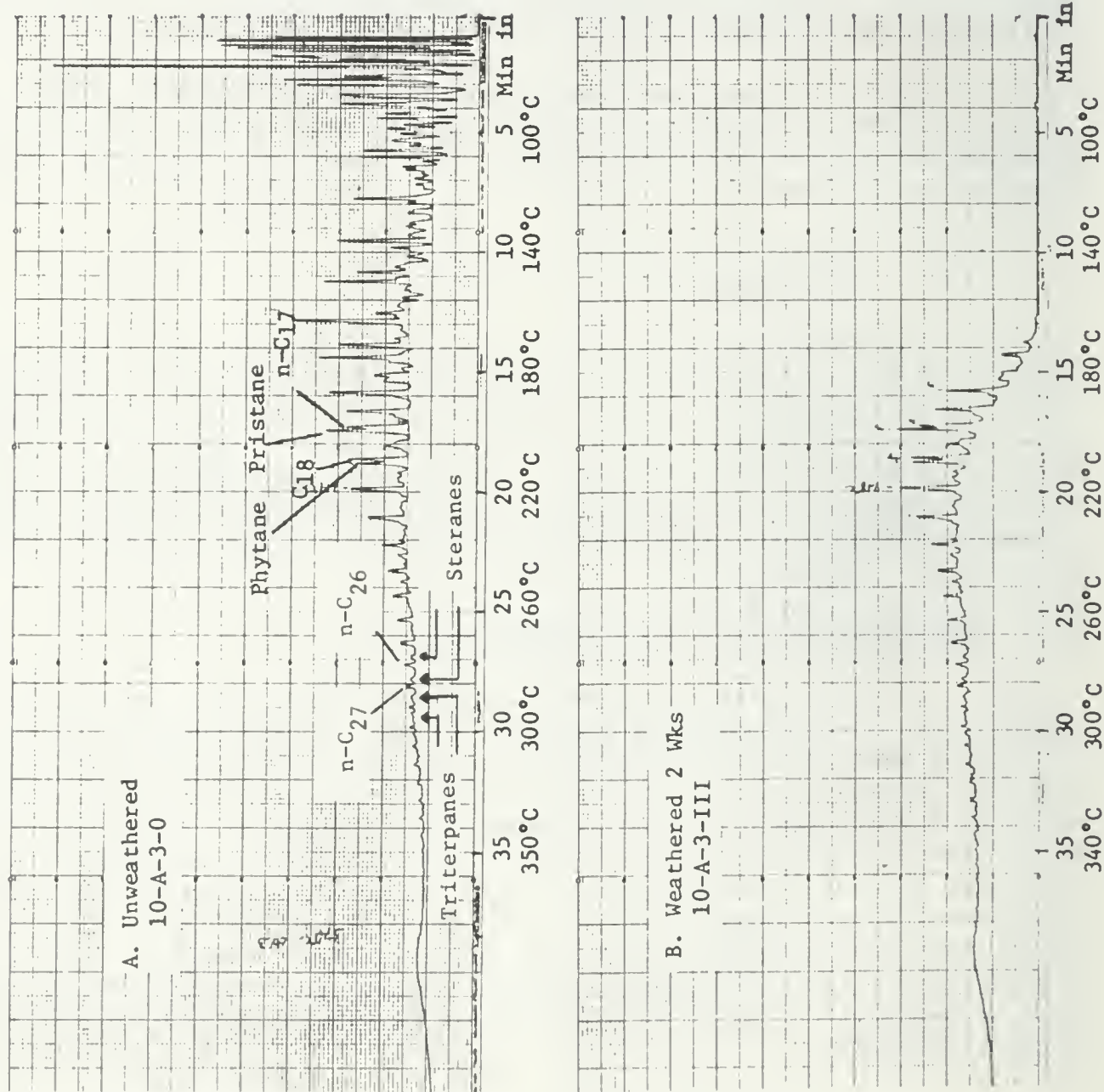
B Phytane

FIGURE 46. GC Fingerprint of Crude Oil 10-A-3-0

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min



IV.6.1 Effect of Weathering on Gas Chromatograms

As expected, weathering effects are quite noticeable in the gas chromatograms of most oil samples and this must be taken into consideration when interpreting them. This is illustrated by Figures 47 and 48 which show the chromatograms of a waxy crude and a fuel oil at various times during weathering. As the traces show, components of the oil below C₁₅ (that is, boiling <520°F) are lost rapidly; after two weeks only traces remain. This is consistent with prior observations (1) and confirms that the part of the chromatogram below this point (i.e., <15 min. retention time) is of little value for identifying an unknown sample with a fresh oil. This points up the need for an artificially weathered, authentic sample for positive identification.

IV.6.2 GC Characteristics of Broad Categories of Petroleum Products

In the same manner as GC distillation traces (Subsection IV.3.2) the more highly resolved GC fingerprints may be used to classify many types of oils.

In some cases the sample can be classified at a glance. For example, crude oils (Figures 46,47,49-51) show a characteristic, smooth distribution throughout the entire boiling range. Blended residual fuels (Figures 52-54 and Navy Special Fuel, Figure 92), on the other hand, usually exhibit a bimodal chromatogram with a second peak at long retention times. Distillate fuels (Figures 48, 55, 56 and Navy Distillate, Figure 91) are lighter and have a much more narrow boiling range. Other highly refined products such as lubricating oils (Figure 57) and white oils (Figure 58) also have a narrow distribution but at much longer retention times.

Gas chromatograms are especially useful in differentiating crudes, blended resids and light distillates but fail to classify heavy material such as lubes and white oils and cannot readily distinguish between diesels and heating oils. In this respect the technique is a natural complement to infrared spectroscopy. The IR method cannot distinguish between weathered crudes and residual fuels but readily classifies lubes, white oils and can sometimes aid in differentiating diesels and light heating oils.

IV.6.3 GC Fingerprinting as a Tool for Positive Identification

This is the area of greatest application for gas chromatography. If authentic samples of suspect sources are available the spill can often be identified. As mentioned above, it is best either to weather these authentic samples or to ignore that part of the chromatogram eluting before about 15 minutes retention time. Good indices for identification are pristane and phytane (17.5 and 18.8 min. retention times (1,29), and the steranes and triterpanes which elute at about 27-30 min. (33). These are shown in Figures 46A and 51B).

FIGURE 47. Effects of Weathering on GC Trace of a Crude Oil, 10-A-2

Column: 15', 1/8", 3Z SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

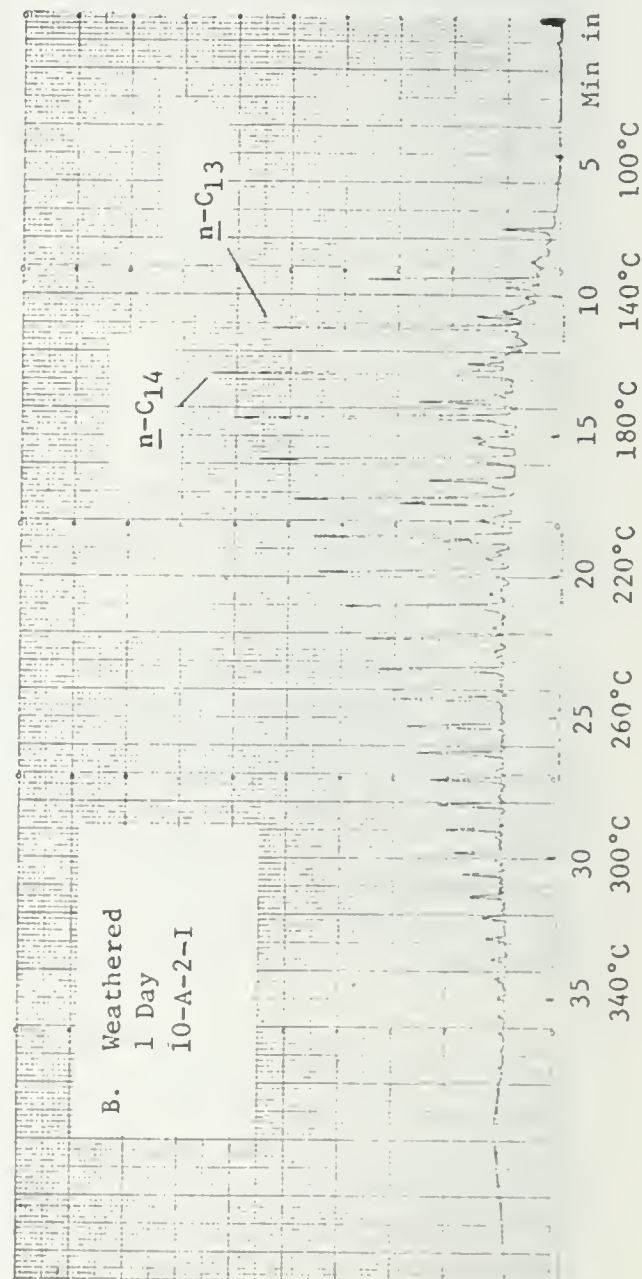
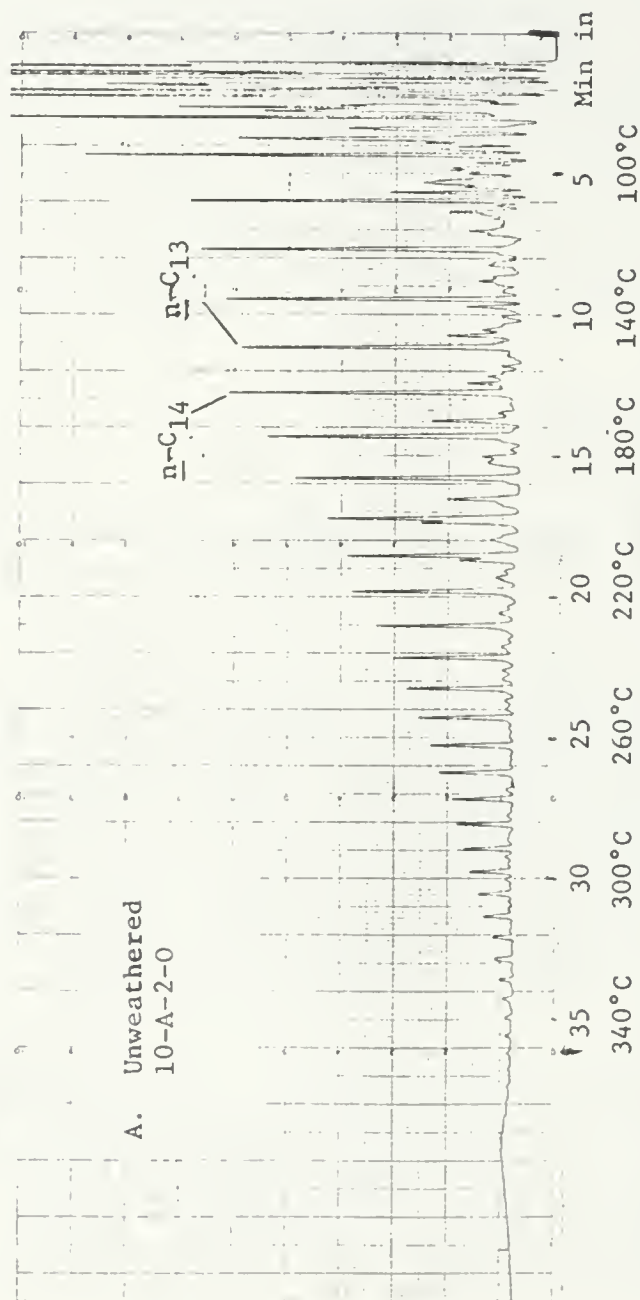


FIGURE 47. (Cont'd.)

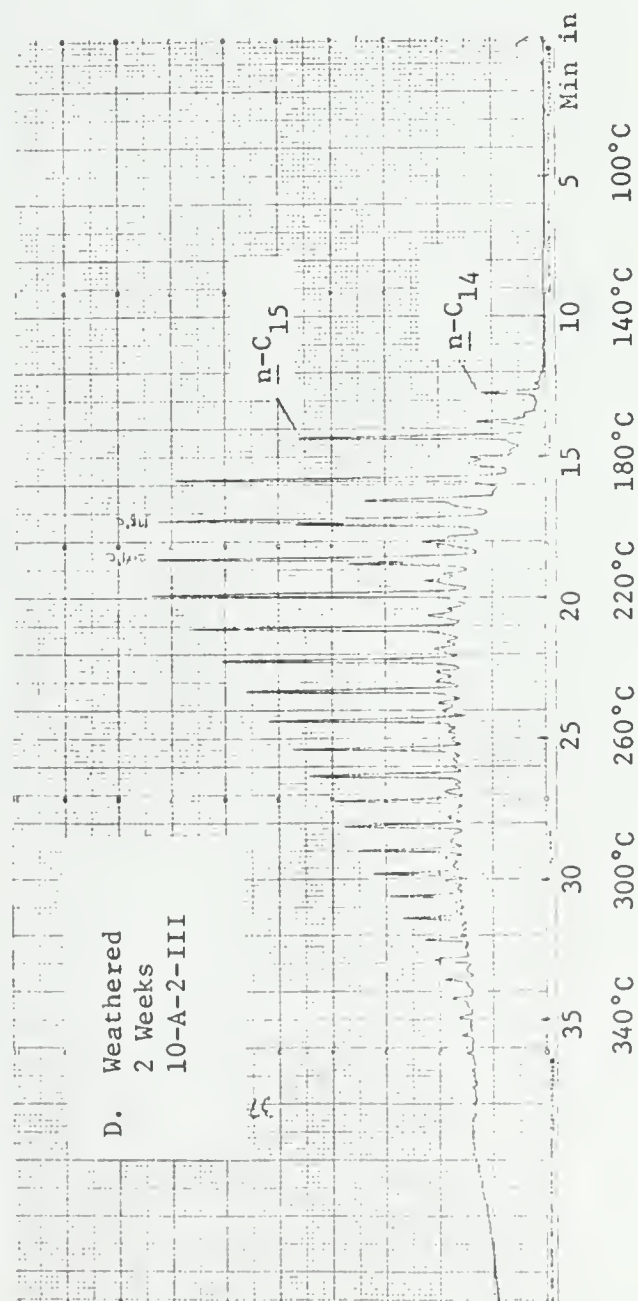
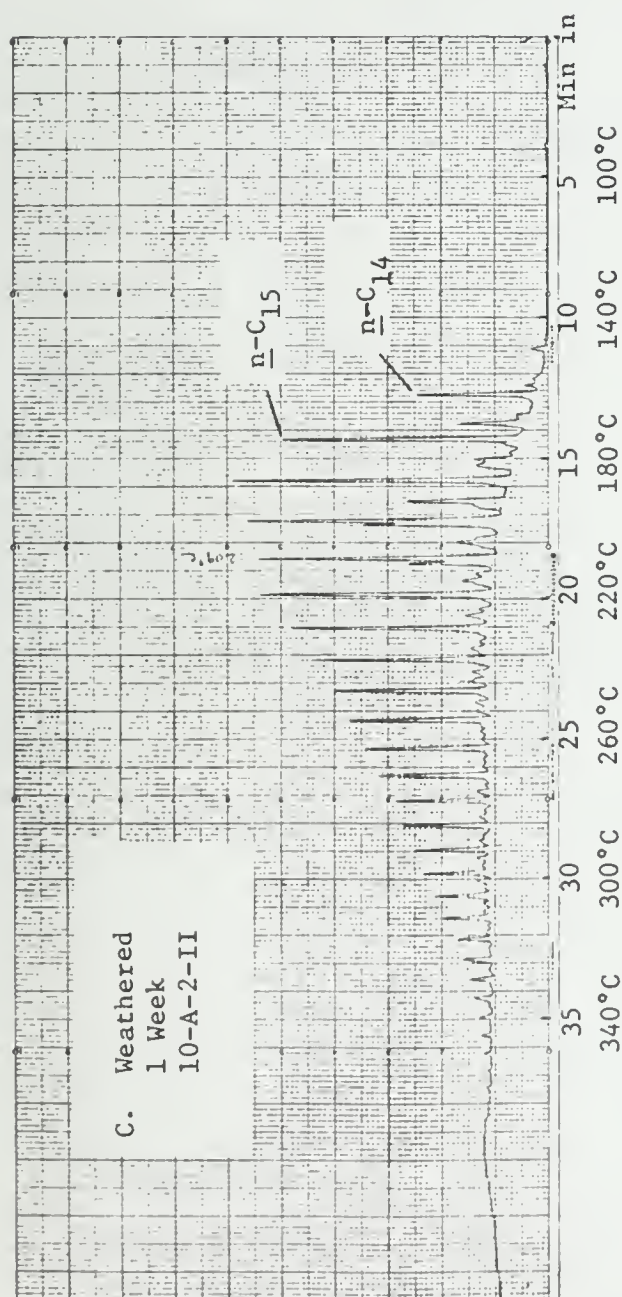


FIGURE 48. Effects of Weathering on GC Traces of a No. 2 Heating Oil, 40-A-1

Column: 15', 1/8", 3X SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1 1/2"/min

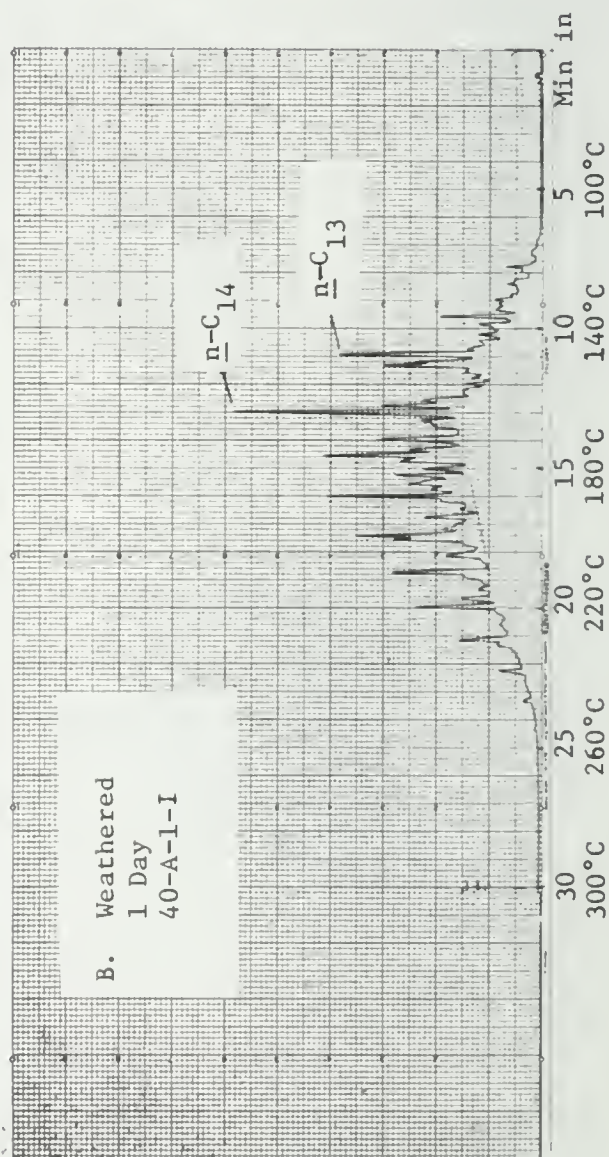
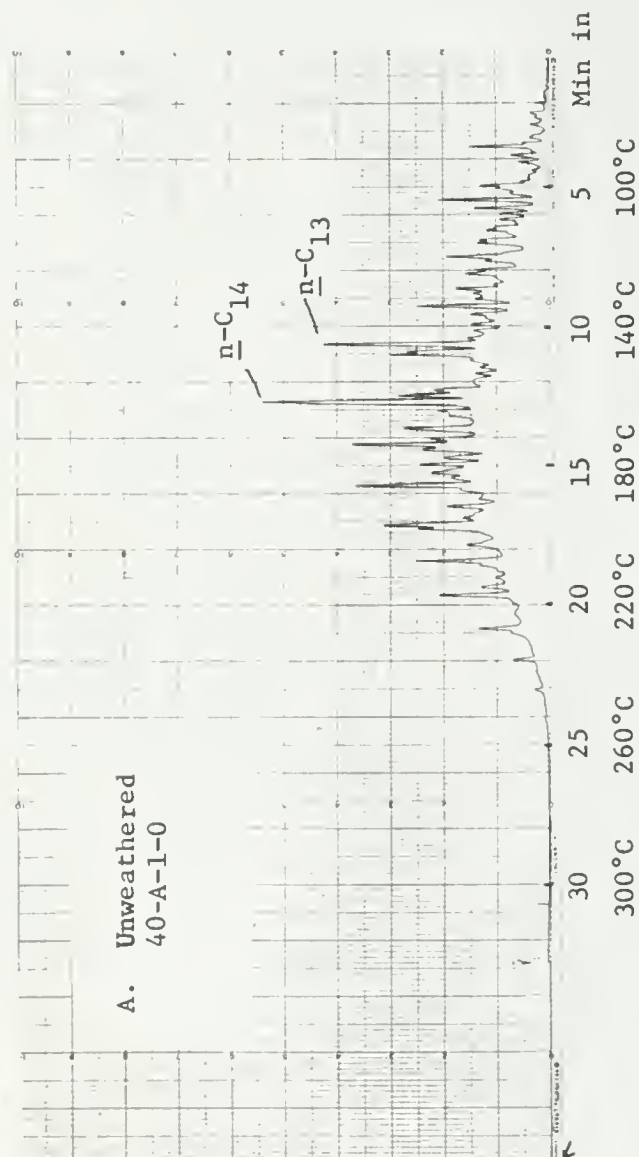


FIGURE 48. (Cont'd.)

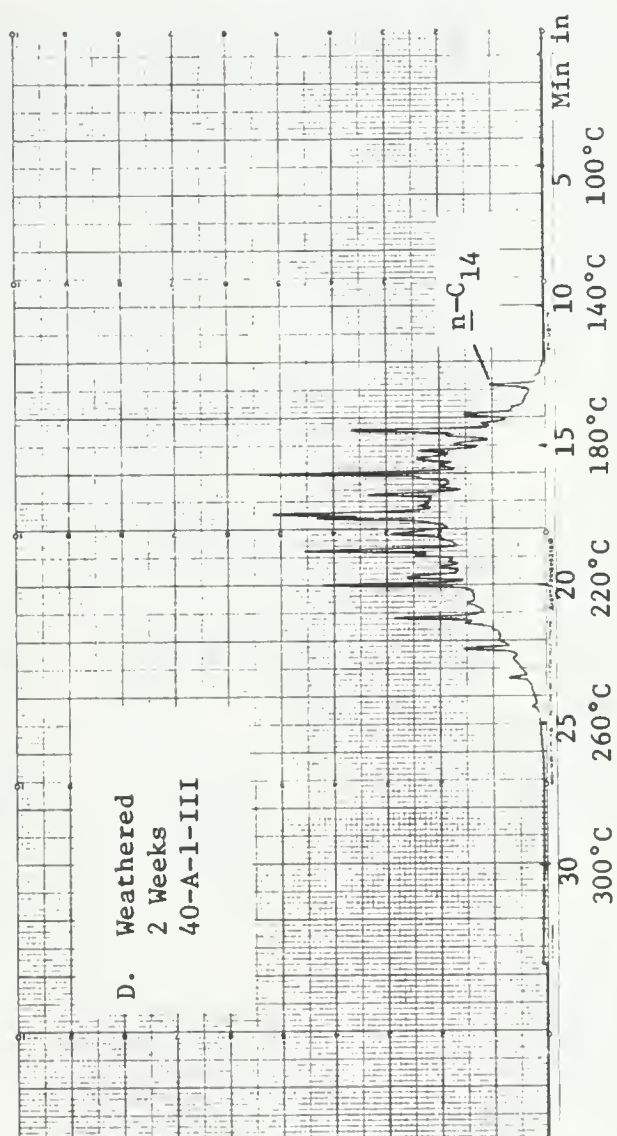
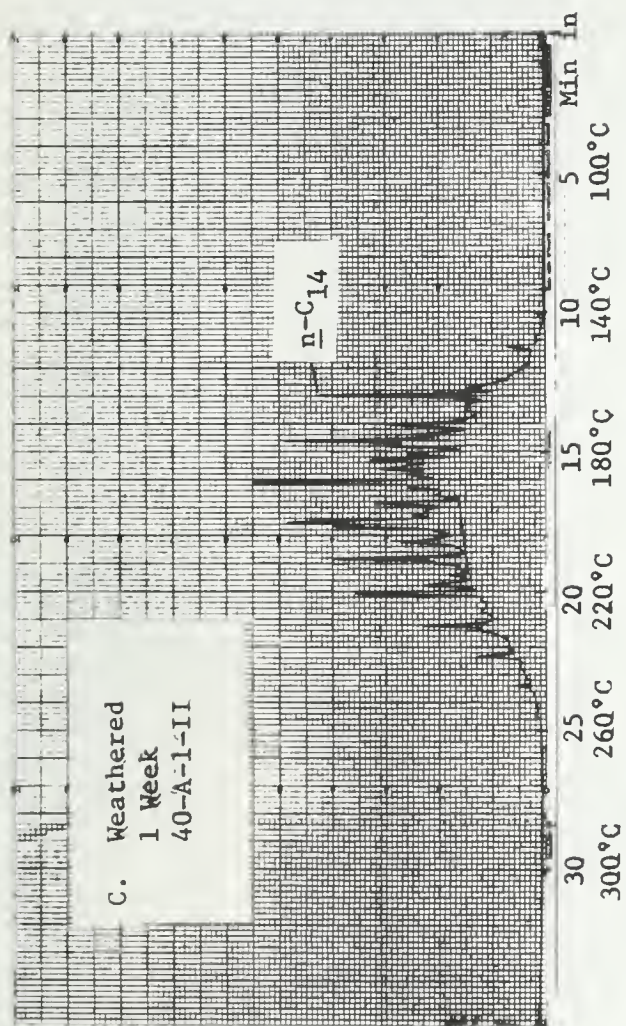


FIGURE 49. GC Fingerprint of Crude Oil 10-A-7

Column: 15', 1/8", 3Z SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1 1/2"/min

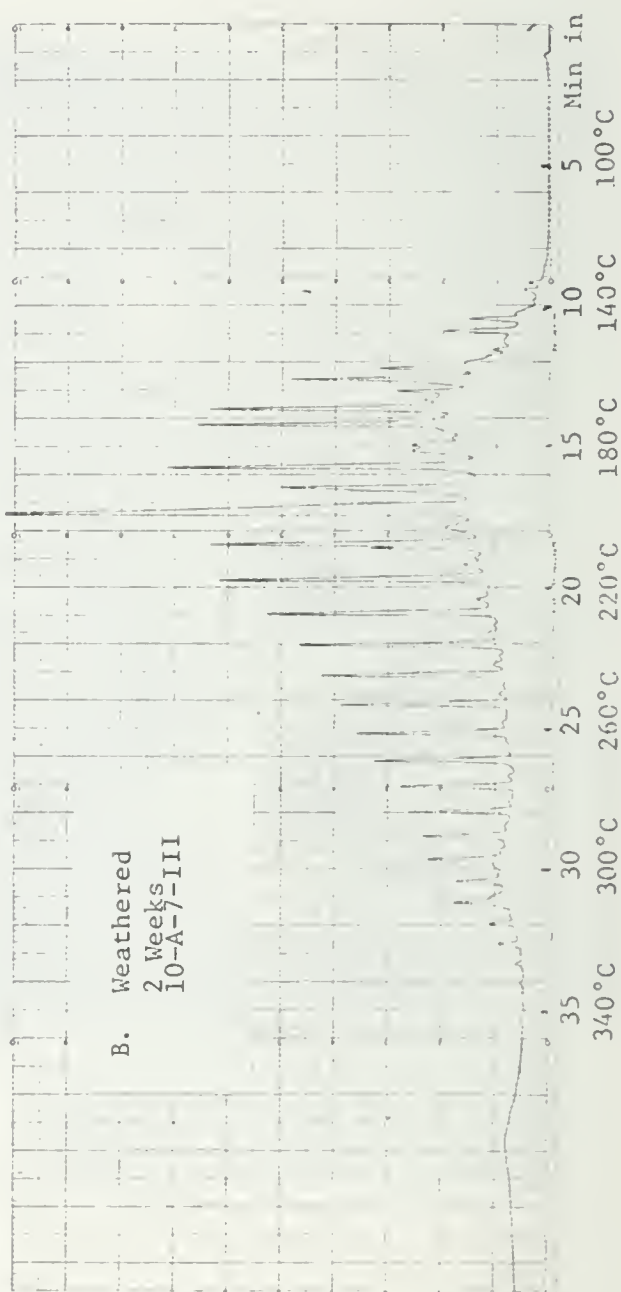
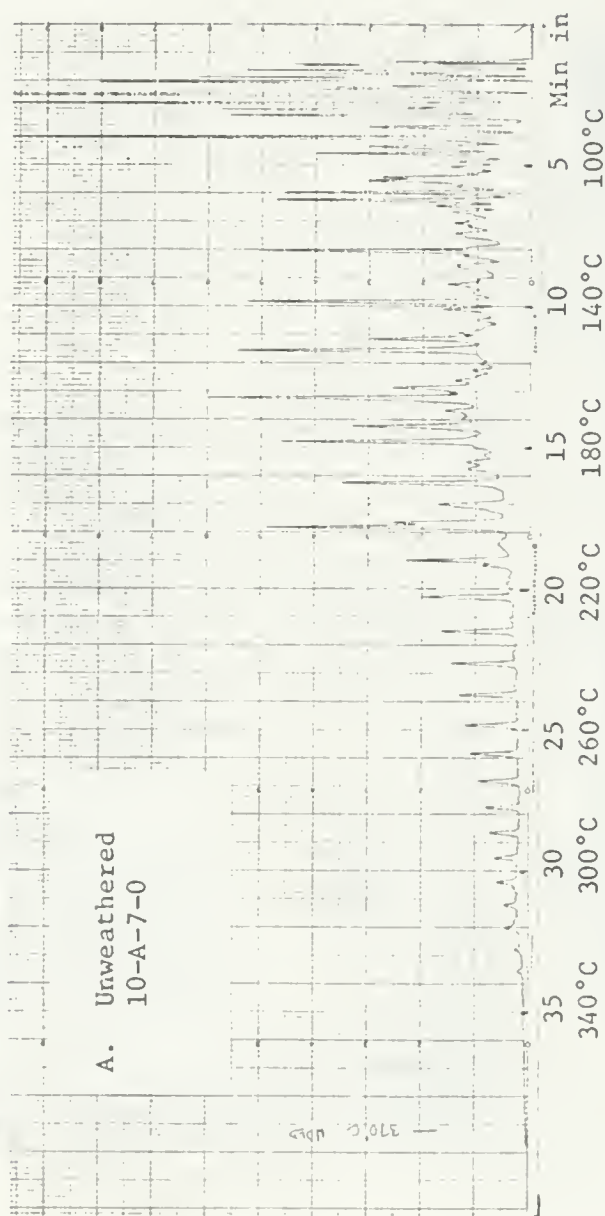


FIGURE 50. GC Fingerprint of Crude Oil 10-A-9

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

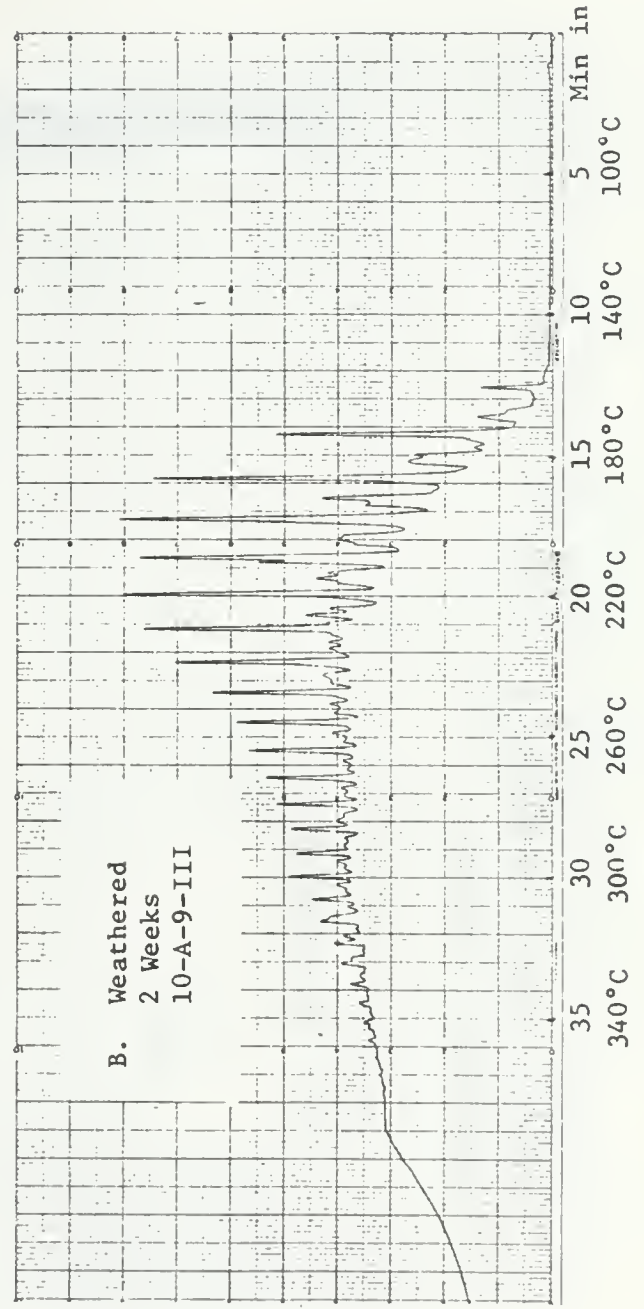
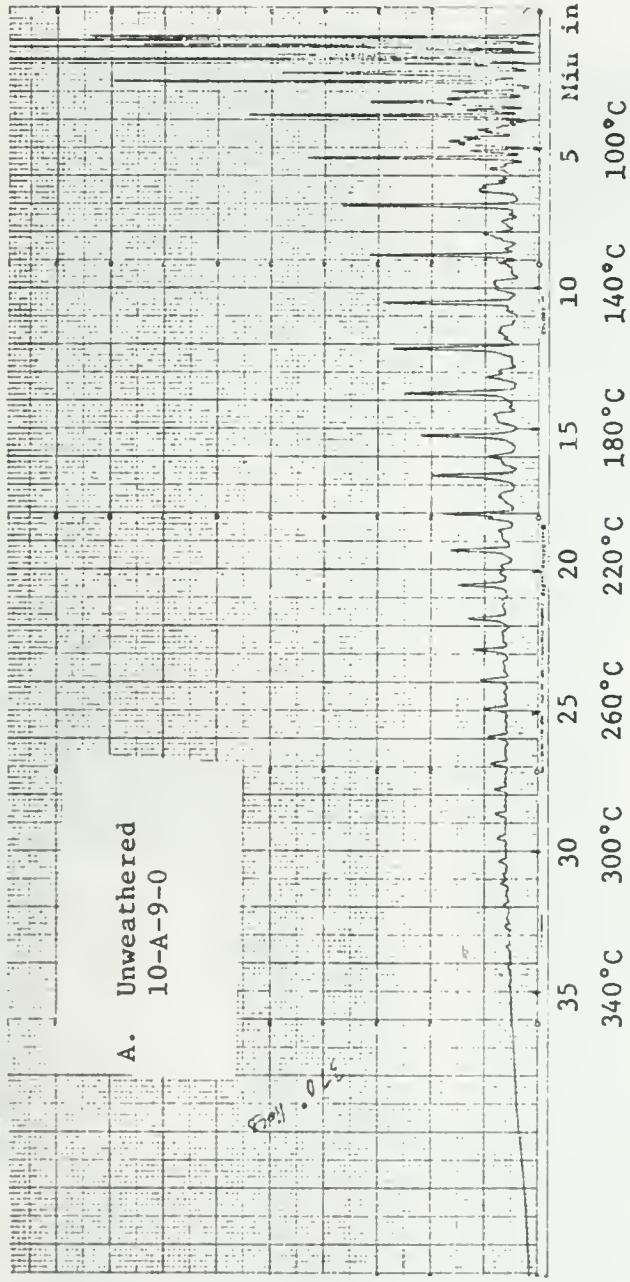


FIGURE 51. GC Fingerprint of Crude Oil 10-A-10

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1 1/2"/min

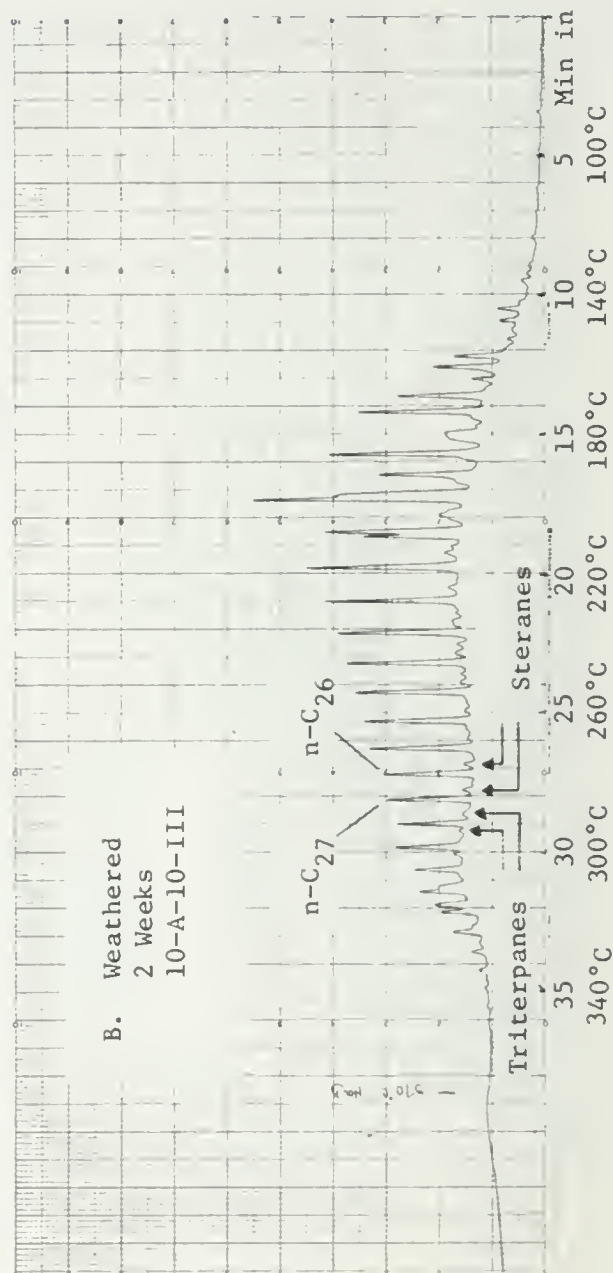
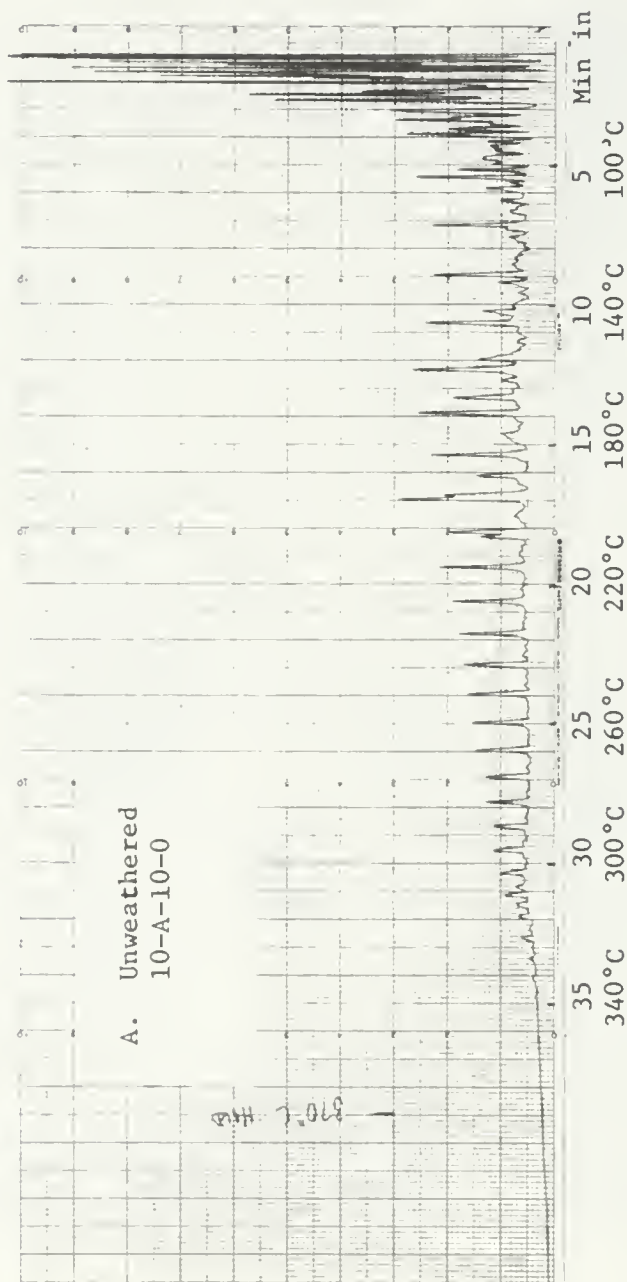


FIGURE 52. GC Fingerprint of No. 6 Fuel Oil (Blended Resid) 32-H-1

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

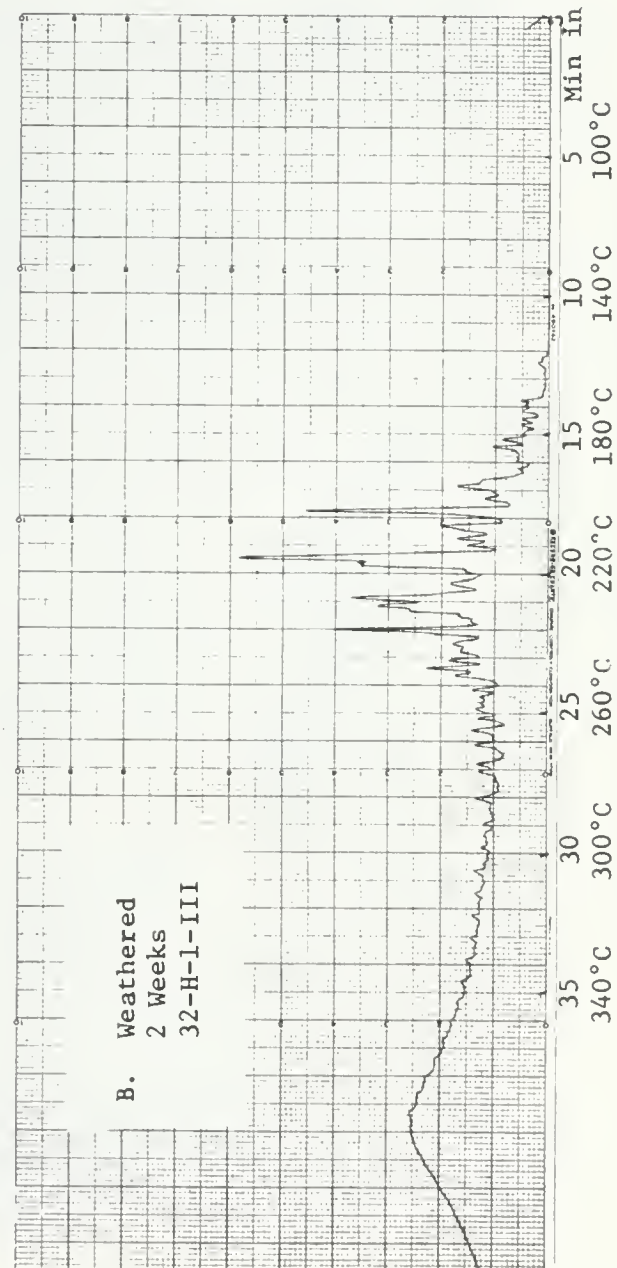
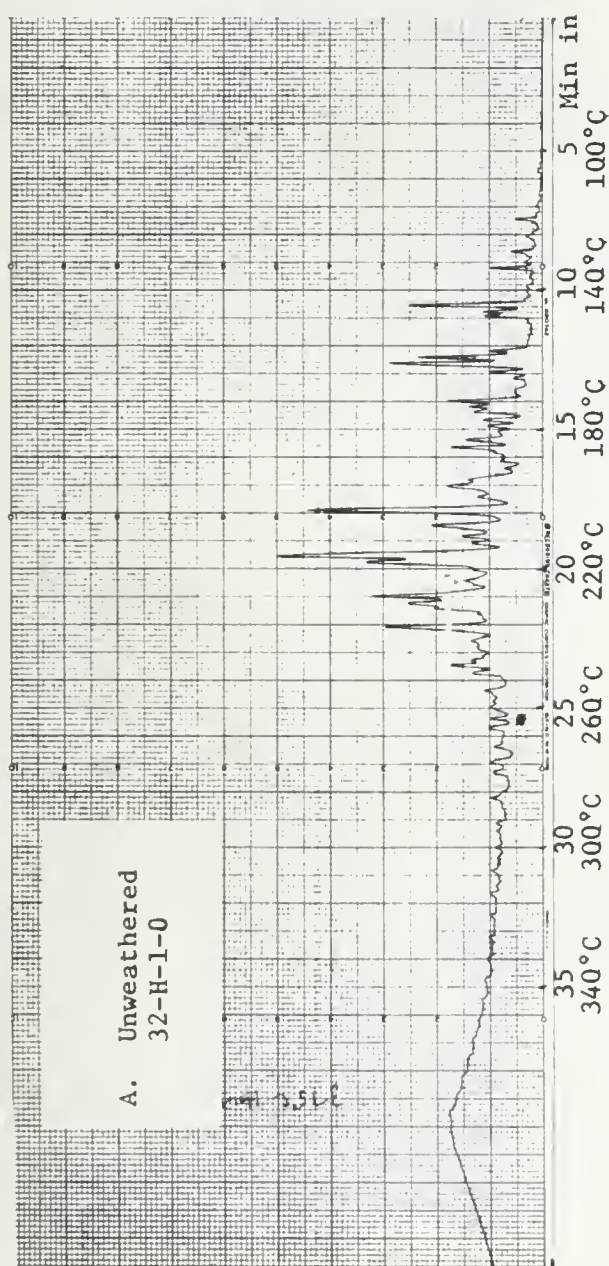


FIGURE 53. GC Fingerprint of Bunker "C", 20-A-1

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

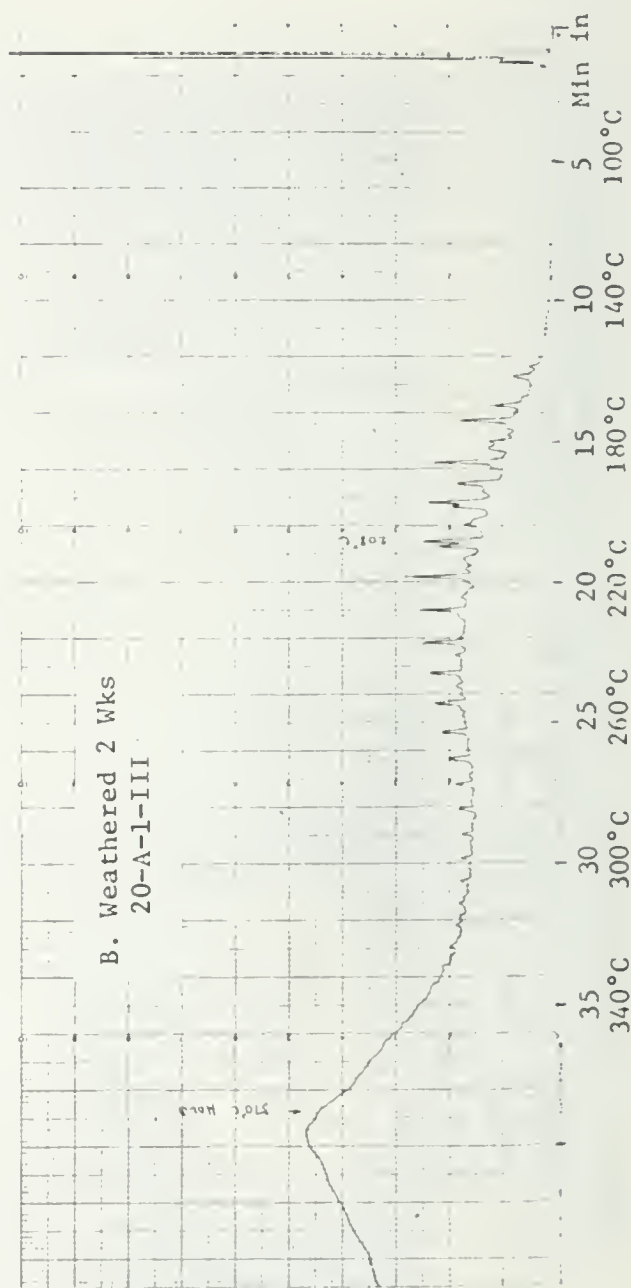
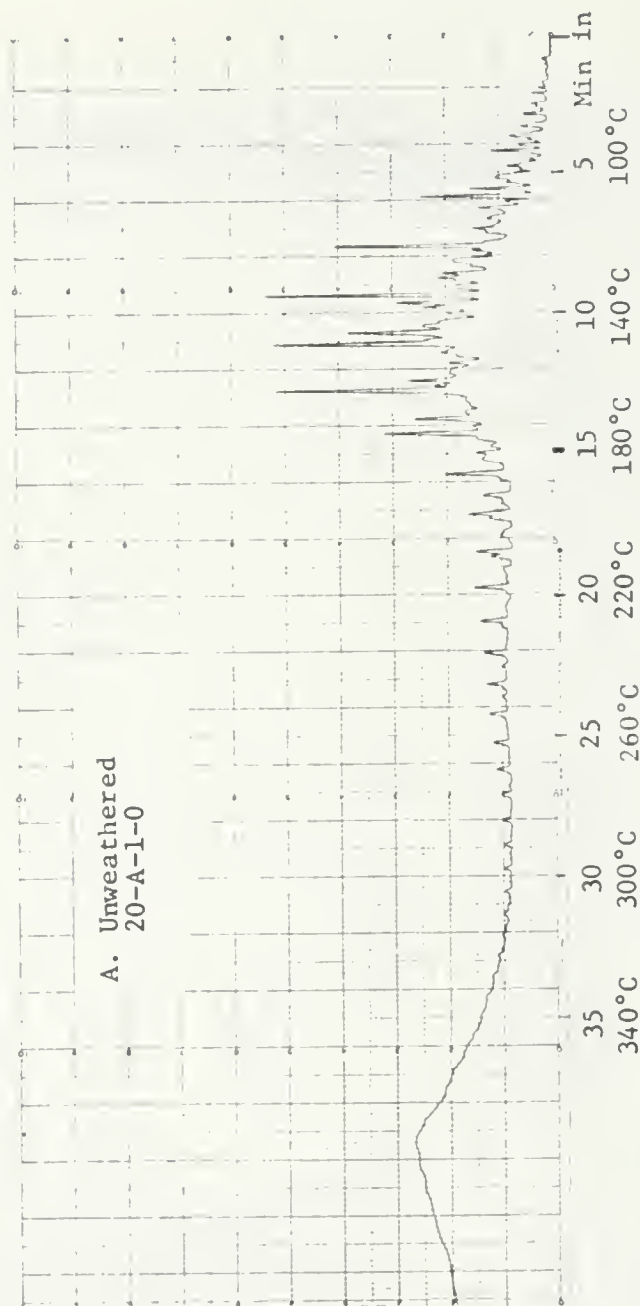


FIGURE 54. GC Fingerprint of No. 6 Fuel Oil 32-F-1
Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport
Program: 60°C - 370°C, 8°/min
Chart Speed: 1/2"/min

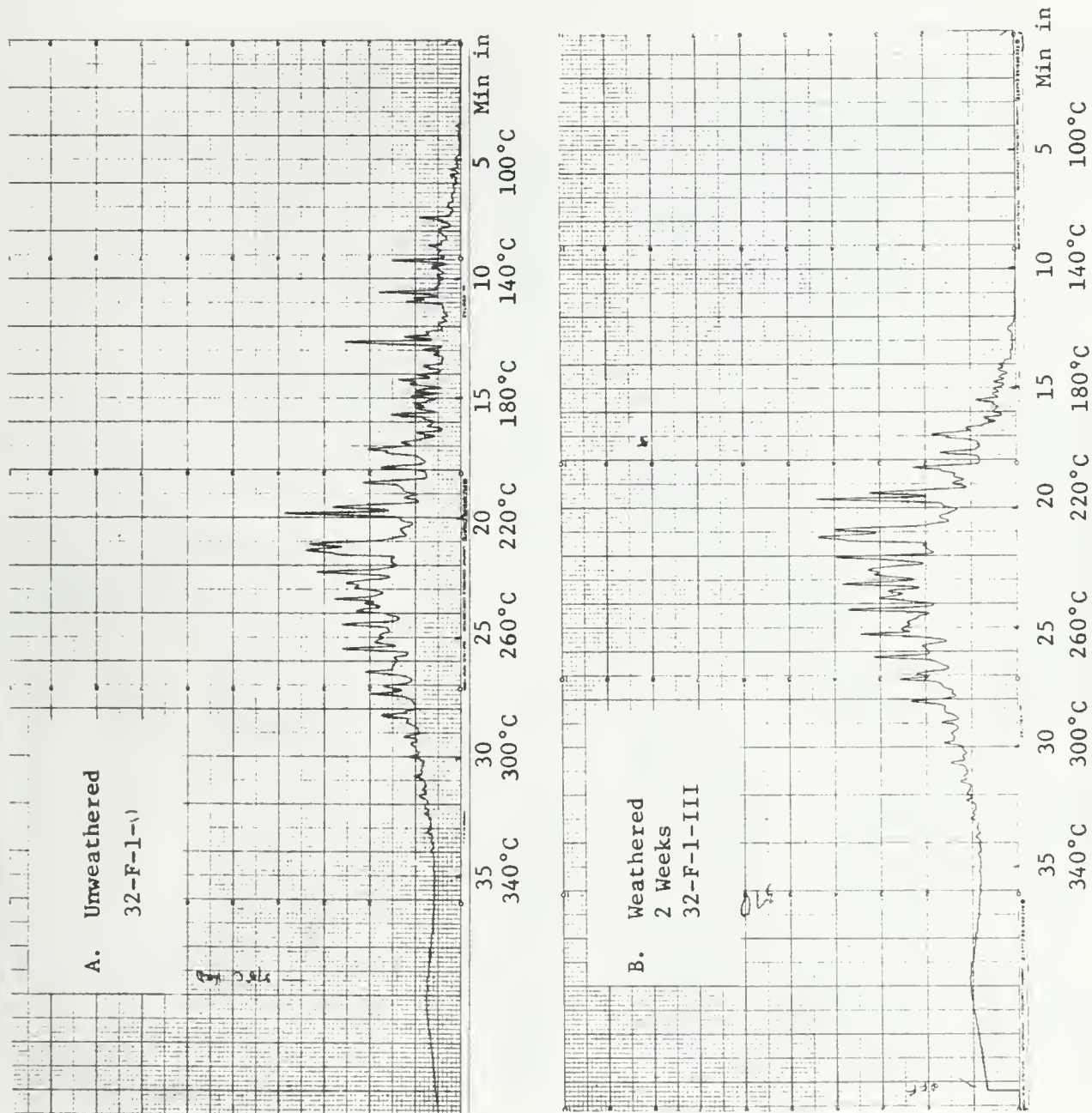


FIGURE 55. GC Fingerprint of Automotive Diesel 42-A-2

Column: 15', 1/8", 3Z SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

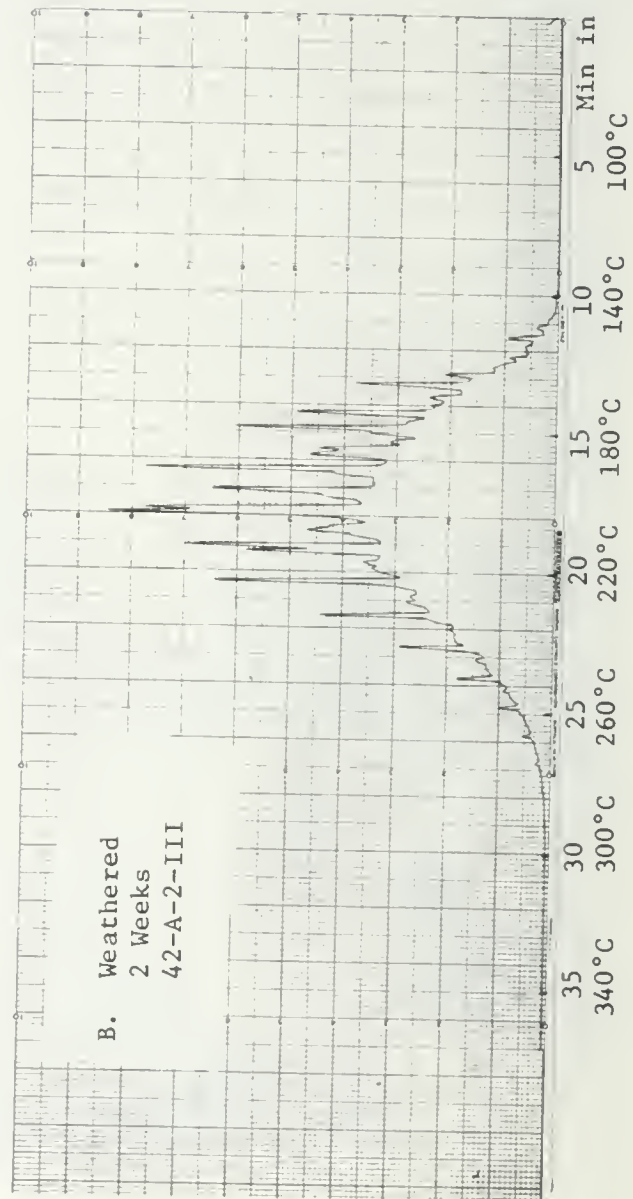
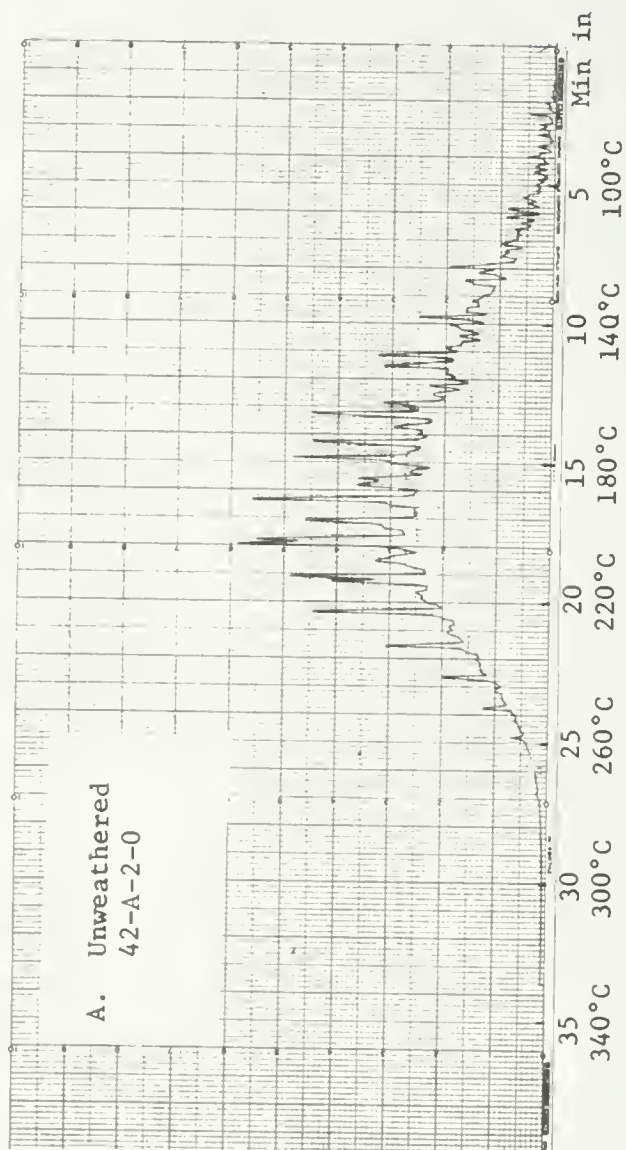


Figure 56. GC Fingerprint of No. 2 Heating Oil 40-B-1

Column: 15', 1/8", 3Z SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

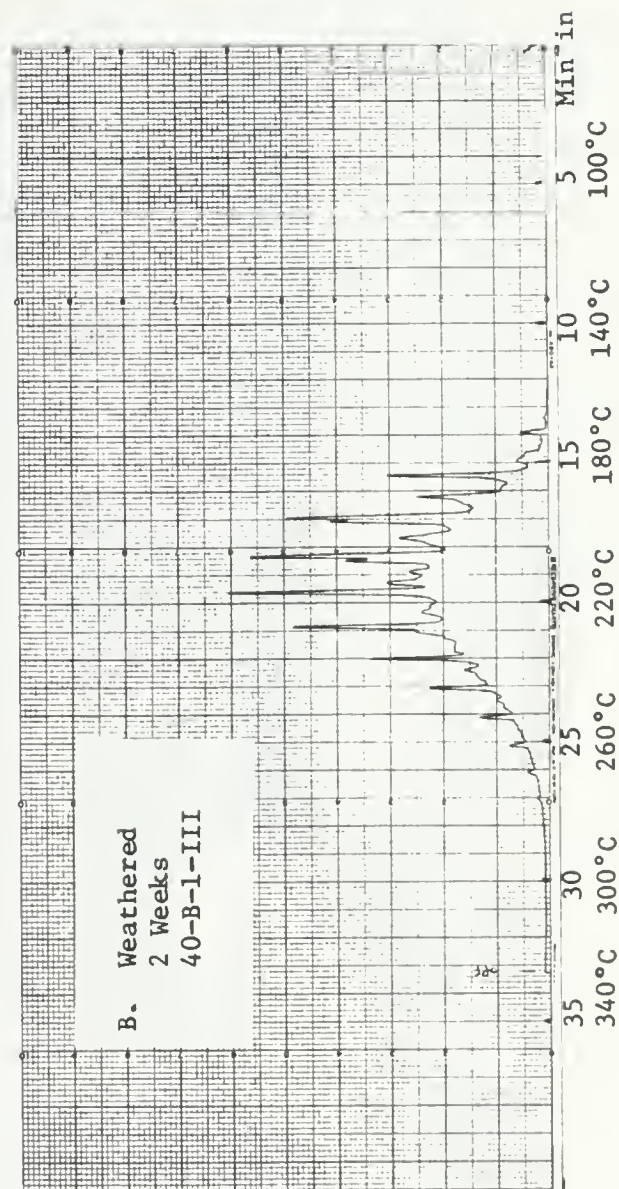
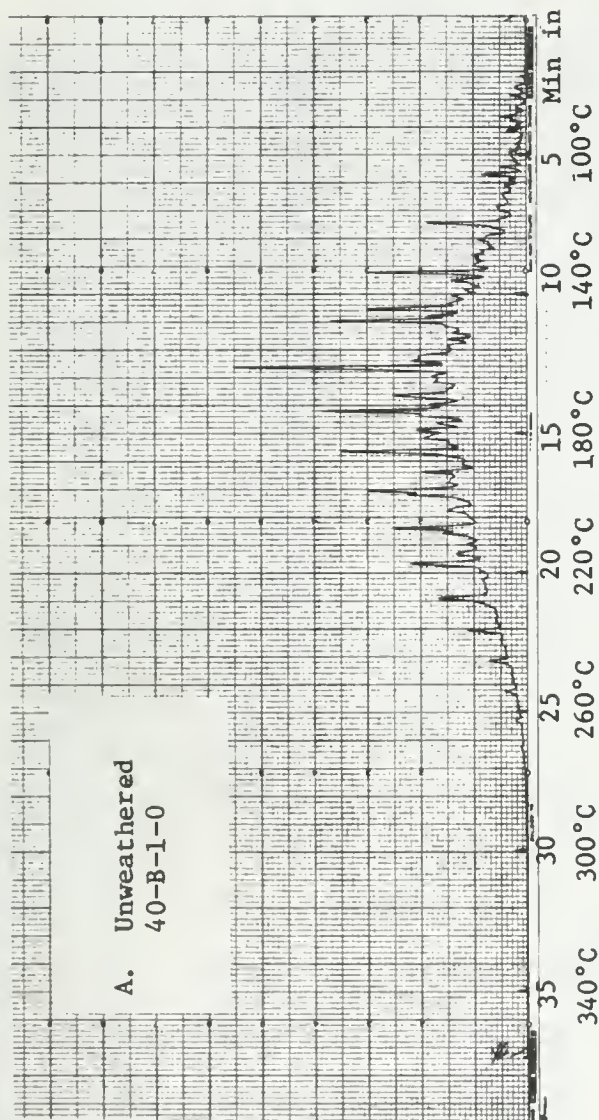


FIGURE 57. GC Fingerprint of Lube Oil, 50-G-2

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

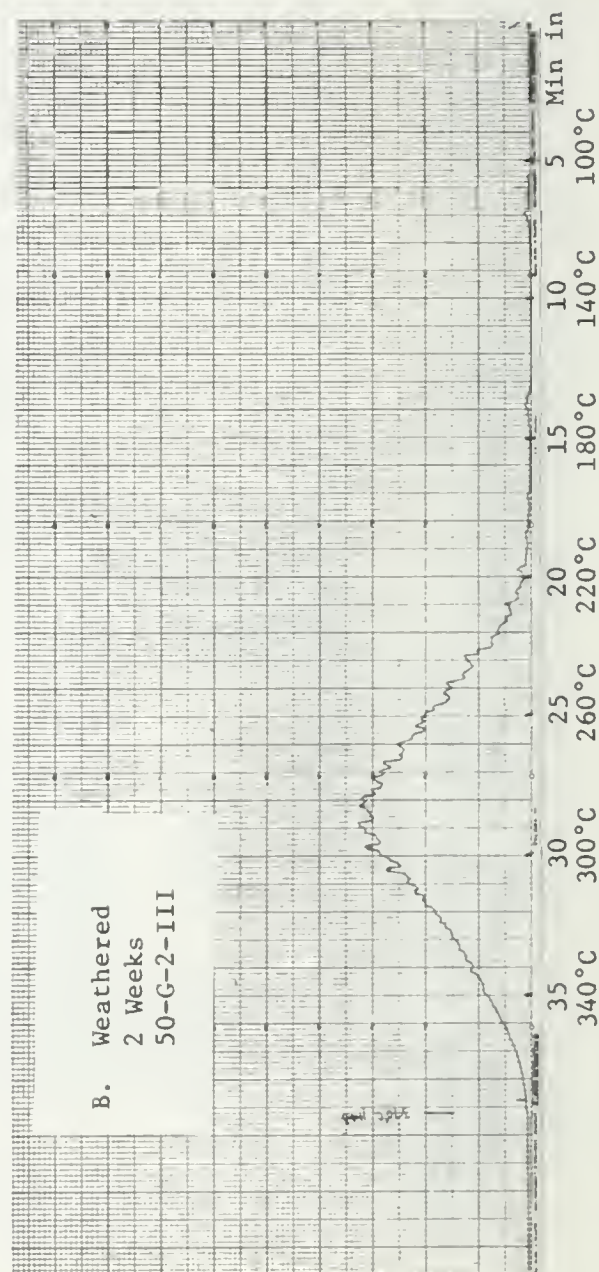
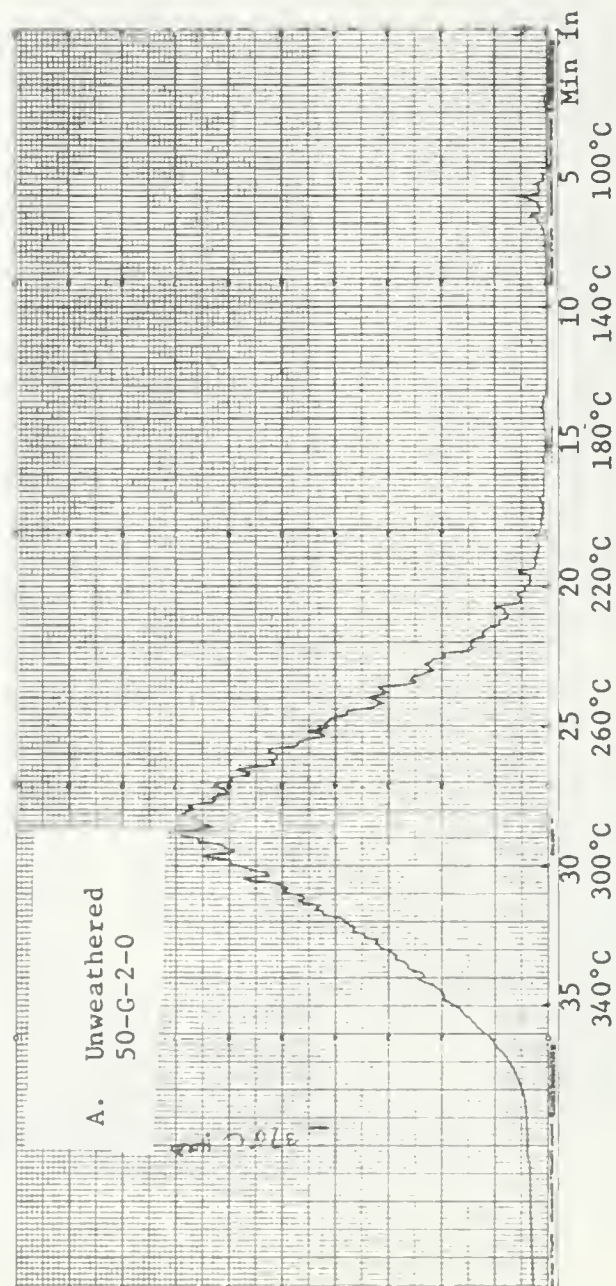
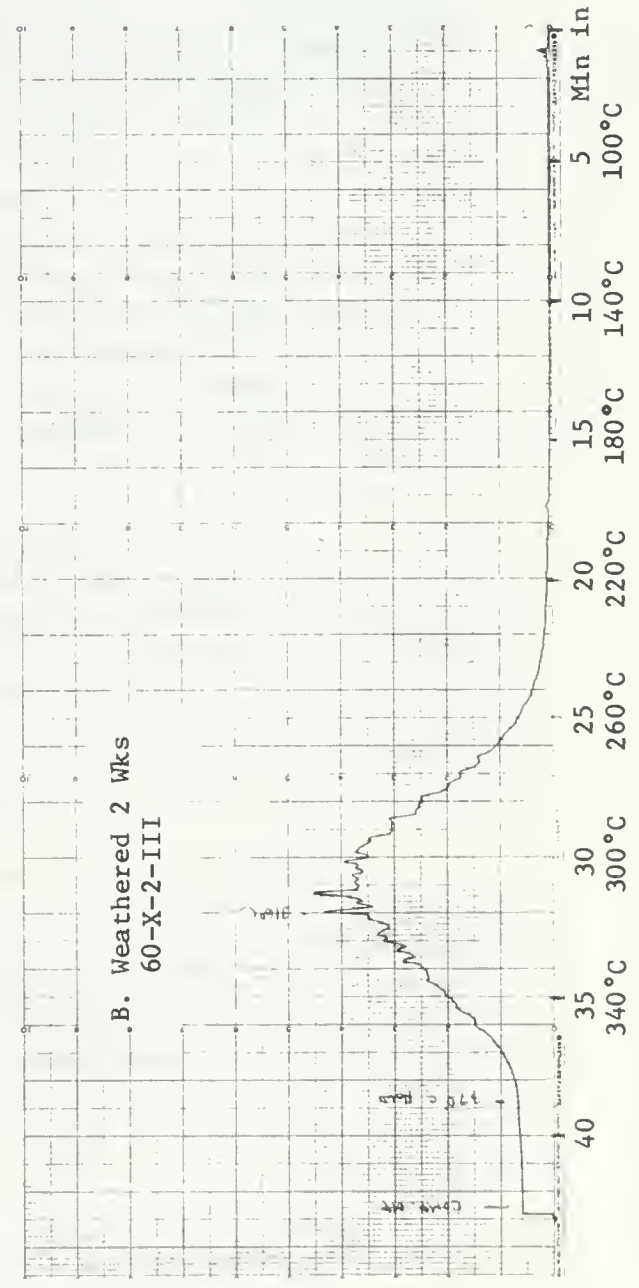
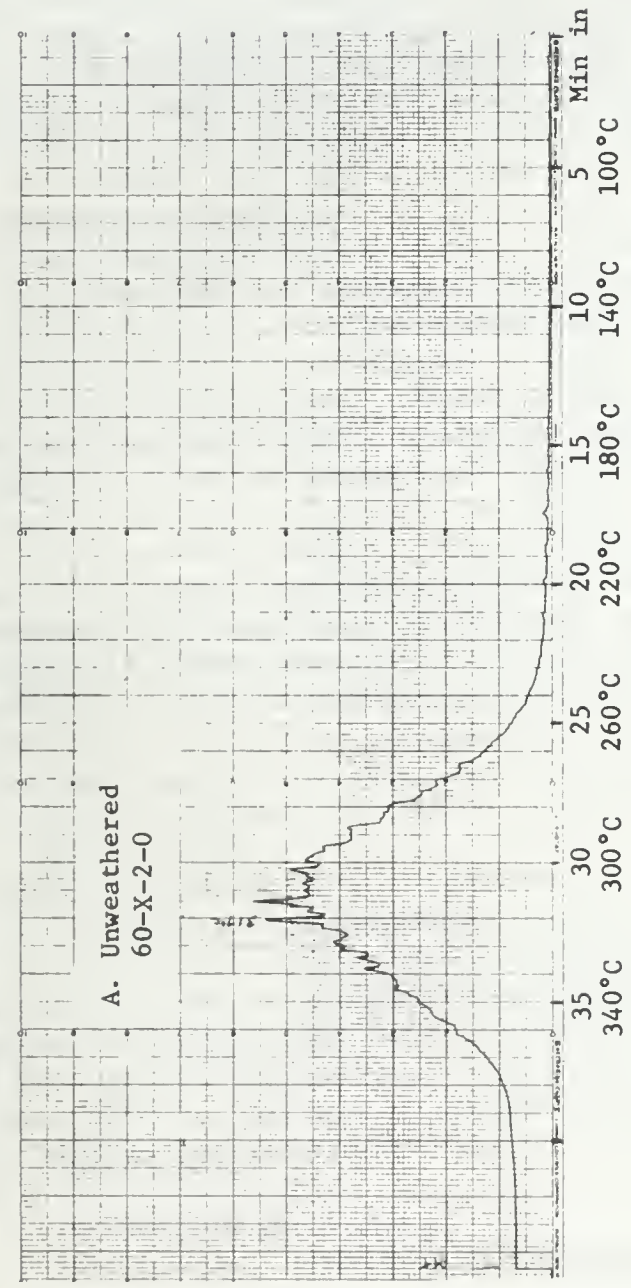


FIGURE 58. GC Fingerprint of White Oil 60-X-2

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min



Examination of the five crude oil chromatograms shown here (Figures 46, 47, 49-51) reveals several significant differences. Crudes 10-A-2 (Figure 47) and 10-A-7 (Figure 49) are much more paraffinic than the others as shown by the sharp n-paraffin spikes rising well above the aromatic-naphthene "envelope". This is apparent in either the weathered or unweathered traces. Contrast the heavier, aromatic crude, 10-A-3 (Figure 46). The paraffinic crudes are easily distinguished by their relative amounts of pristane (17.5 min. retention time). The pristane content of 10-A-7 (Figure 49) is abnormally high, the peak rising well above that of the C₁₇ hydrocarbon which elutes just before it. On the other hand, the phytane peak (18.8 min.) is significantly smaller than the C₁₈ spike immediately preceding it. In 10-A-2 (Figure 47) both pristane and phytane peaks are greatly reduced relative to the nearby paraffins, with the pristane peak significantly more intense than phytane.

In contrast, the aromatic crude, 10-A-3, shows pristane and phytane at about the same concentrations as each other and the adjacent paraffins. This crude, in addition, has unusually large concentrations of steranes and triterpanes relative to C₂₇-C₃₀ paraffins (Figure 46).

The other two crudes (10-A-9 and 10-A-10, Figures 50 and 51) are superficially somewhat similar. On closer examination, significant differences are apparent. The crude 10-A-10 shows a greater quantity of heavier paraffins eluting beyond 25 minutes and the paraffin/sterane or triterpane ratio is higher. The pristane/C₁₇ ratios are reversed in these crudes, with 10-A-9 having more C₁₇ than pristane. These differences are apparent both in the weathered and unweathered samples.

Similar comparisons can be drawn in order to differentiate the various residual fuels (Figures 52-54) as well as the distillate fuels (Figures 48, 55, 56, Navy Distillate, Figure 92). Inspection of relative peak heights clearly distinguishes these materials. The lube oils are more difficult to distinguish because of the poor resolution obtained in chromatographing these heavy materials. Weathering does not affect these materials to any way observable in the GC. Both TLC and IR techniques are useful in identifying these types of oils and serve to confirm and extend GC findings.

IV.6.4 Use of GC Peak Ratios

The characteristics discussed in the previous subsection can be applied to identification in a more quantitative manner by ratioing certain GC peaks. Especially useful are pristane, phytane and the nearby n-paraffins, although a variety of other peaks can be used as well (29). Pristane and Phytane are naturally occurring isoprenoids present in nearly all crudes. They are probably derived from chlorophyll (29). They are useful for distinguishing petroleum from animal-derived oils, and by measuring their ratios, may provide a useful index for identifying certain types of petroleum products as well. Blumer (29) has pointed out that the relative abundance

of these hydrocarbons varies significantly in crude oils and this is little affected by weathering. Some Pristane/Phytane ratios, determined from GC traces are given in Table 21. These values suggest Blumer is correct, at least to a first approximation. The agreement between values for weathered and unweathered samples is fairly good and could be improved by optimizing GC conditions (i.e., averaging several analyses). Most oils show significant differences in at least one of the ratios shown. This method, however, cannot be applied to heavy fuels, lube oils, etc., where these materials are not present or are poorly resolved.

IV.7 Thin-Layer Chromatography

Our work in TLC was designed as a feasibility study to determine whether this technique could be developed into a useful, simple method for rapidly classifying petroleum products. Based on results obtained so far, this expectation has been fully realized and surpassed. TLC may become the method of choice for classification and will even be uniquely useful for certain aspects of identification as well.

The present work, being a feasibility study, was aimed at determining the value and limitations of the method with respect to resolving power, reproducibility, and to get some idea of the types of adsorbents and eluting solvents which would prove most useful. From these preliminary studies, the following systems were rated as to usefulness

A. Adsorbents

Most Useful

Silica gel 60F-254*

Useful in Conjunction with Silica Gel Plates

Alumina GF**

Of Little Use

Cellulose F

Silica gel coated with hexadecane

B. Eluting Systems

Most Generally Useful

n-Hexane - Glacial Acetic Acid (50:1)

n-Hexane - Cyclohexane - Glacial Acetic Acid (4:1:trace)

* Obtained from Scientific Glass Apparatus, Inc., Bloomfield, New Jersey.

** Obtained from Analtec Inc., Wilmington, Delaware.

Table 21

GC Peak Ratios for Some
Weathered and Unweathered Oils

<u>Sample</u>	<u>Type of Oil</u>	<u>Weathering Time</u>	<u>Pristane/ Phytane</u>	<u>C₁₇/ Pristane</u>	<u>C₁₈/ Phytane</u>
10-A-2-0	Crude	0	1.7	2.0	2.9
10-A-2-III	Crude	2 wks.	1.5	1.8	2.6
10-A-3-0	Crude	0	1.7	0.79	1.1
10-A-3-III	Crude	2 wks.	1.5	0.76	1.1
10-A-7-0	Crude	0	7.9	0.47	3.4
10-A-7-III	Crude	2 wks.	--	--	2.5
10-A-9-0	Crude	0	0.88	3.2	2.7
10-A-9-III	Crude	2 wks.	0.98	2.4	2.0
10-A-10-0	Crude	0	2.8	0.65	1.7
10-A-10-III	Crude	2 wks.	2.2	0.62	1.9
40-A-1-0	No. 2 Oil	0	3.3	1.1	3.5
40-A-1-III	No. 2 Oil	2 wks.	3.2	1.3	3.6
40-A-2-0	No. 2 Oil	0	2.2	1.2	2.3
40-A-2-III	No. 2 Oil	2 wks.	2.1	1.1	2.6
40-B-1-0	No. 2 Oil	0	2.0	1.6	2.5
40-B-1-II	No. 2 Oil	1 wk.	1.6	1.4	2.2
40-B-1-III	No. 2 Oil	2 wks.	1.5	1.4	2.2
40-H-1-0	No. 2 Oil	0	2.0	1.2	1.7
40-H-1-II	No. 2 Oil	1 wk.	1.4	1.0	1.3
40-H-1-III	No. 2 Oil	2 wks.	1.7	1.0	1.5
42-A-1-0	Diesel	0	2.5	1.3	2.3
42-A-1-III	Diesel	2 wks.	2.1	1.2	2.1
42-A-2-0	Diesel	0	1.9	0.89	1.4
42-A-2-III	Diesel	2 wks.	2.0	0.96	1.4
42-A-3-0	Diesel	0	1.0	1.4	1.3
42-A-3-III	Diesel	2 wks.	0.99	1.3	1.2

Useful in Conjunction with Above

n-Hexane
Cyclohexane

C. Visualizing Agents

Useful

Long Wave UV light (3600 Å)
Short Wave UV light (2500 Å)
Iodine Vapors
con. H₂SO₄ - Dichromate + Charring

In general, we have had good results only with solvents of poor eluting power. A small amount of acetic acid added to them gives some different patterns which are also useful. Activating the plates by heating had very little effect. Saturating the chromatographic chamber with solvent vapors greatly reduced the development time and eliminated "edge effects"* but also gave poorer resolution. It is generally better to use unsaturated chambers (17, 36).

IV.7.1 TLC as a Classification Tool

This method may be used to classify oils on the basis of two observations.

- The characteristic pattern of spots.
- The response of the spots to different visualizing agents.

This is based on the fact (Section I) that broad classes of petroleum products have different amounts of chemical types which respond variously to different adsorbents, eluting solvents and visualization methods. For example, crudes, which contain all types of compounds found in oils travel as one long smear of broad zones which are visualized by all types of agents. Refined products, which have some of these materials removed have a tendency to form discrete zones which respond to short but not long wave ultraviolet radiation. A summary of generalized responses is given in Table 22. Some possible structural assignments responsible for these zones are given in Table 23.

IV.7.2 TLC as a Classification Technique

The results of our feasibility study indicate this technique may be developed into a useful tool for classifying an unknown spill sample even in the absence of an authentic sample.

* The tendency for spots at the edge of the plate to travel faster.

Table 22

GENERALIZED RESPONSE OF VARIOUS
TEST OILS TO VISUALIZING REAGENTS

Type of Oil	Type of Spots	Response to Visualizing Agent			Iodine Vapor
		Short Wave UV ²	Long Wave UV ³	H ₂ SO ₄ ⁴	
Crude	Long smear	Blue (I)	Blue (I)	Chars	Red-Brown
Distillate Fuel	Discrete Zones	Grey (M)	None ⁵	Chars	Red-Brown
Motor Lube Oil	Discrete Zones	Grey (F)	None	Chars	Red-Brown
Residual Oil	Long Smear	Blue (I)	Blue (I)	Chars	Red-Brown
White Oil	Single Zone	None	None	Chars	Red-Brown

1. I = intense; M = moderate, F = faint.
2. About 2500 Å.
3. About 3600 Å.
4. After heating at 120° for 1/2-1 hr.
5. Strong spots may show very faint blue color.

TABLE 23

SUGGESTED STRUCTURAL ASSIGNMENTS FOR
MATERIALS RESPONSIBLE FOR TLC ZONES(1,2)

Chemical Types	Approximate R _F Ranges ³	Visualized by				Found in Oils				
		Long UV	Short UV	I ₂	H ₂ SO ₄	Crudes	Resid. Fuels	Dist. Fuels	Lube Oils	White Oils
Polar Additives	0-0.20		X	X	X			X	X	
Polynuclear Aromatics	0-0.30	X	X	?	X	X	X			
2-3 Ring Aromatics	0.40-0.60	X ⁴	X		X	X	X	X	X	
Light Aromatics	0.60-0.70		X		X	X	X	X	X	
Naphthenes-Olefins	0.70-0.90		X ⁴	X	X	X	X	X	X	X
Paraffins	0.90-1.0				X	X	X	X	X	X

- - - - -

(1) Not confirmed by use of authentic compounds.

(2) Silica gel plates eluted with n-Hexane: HOAc (50:1).

(3) R_F = $\frac{\text{Dist. from Origin of Spot}}{\text{Dist. from Origin of Solvent Front}}$

(4) Faint spots only; isolated olefins and most naphthenes are not visualized by UV.

The use of TLC in classification of oils is illustrated by Figures 59-64. Here diverse petroleum products are shown chromatographed on silica gel and eluted with hexane-acetic acid. Three different visualizing agents were used. The fourth, long wave UV light could not be photographed. As described above, these systems are all useful and, since only the $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$ system is destructive, each system may be used in turn.

The results of chromatographing some unweathered oils using UV as the visualizing tool is shown in Figure 59. A complete series of 8 weathered oils, representatives of all classes studied, is shown in Figure 60. Photography under UV light is difficult and contrast is much better with the naked eye. Figures 59 and 60, however, serves to illustrate the method. The crude oils, 59A, G and 60A and particularly the heavy residual fuels, 59E and 60E and G, show considerable amounts of heavy and medium aromatics starting at the origin and continuing, unbroken, to an R_F of about 0.60. The distillate fuels, 59B, C and 60B, C, show discrete spots in the aromatic region with the No. 2 heating oil 59B, 60B more intense. The presence of additives near the origin, is also apparent with the No. 2 but absent in the diesel. The lube oil, D in both figures, shows only a faint spot, visible in the UV, in this region. As expected, the white oil, 59 and 60F, having no aromatics, shows no absorption. These patterns appear somewhat more clearly in Figure 61, which is the same plate as 60 visualized by spraying with laboratory cleaning solution and charring. The $\text{H}_2\text{SO}_4 - \text{Na}_2\text{Cr}_2\text{O}_7$ system is quite non-selective and most organic compounds are affected. Note that crudes and heavy fuels, 51A, E and G appear as one long zone, although, in the case of the blended resids E and G heavier zones are also apparent. The distillate fuels have several spots or zones at R_F values of 0.4-0.6 with the No. 2 fuel oil showing stronger spots at somewhat lower R_F . This is, again, ascribable to a higher percentage of heavy aromatics. The lube oil, D, is interesting in that the major spot in Figure 61 is at an R_F of about 0.7-0.8 as contrasted to 0.3 in Figure 60. This is quite typical of automotive crankcase lubricants. Lubes have few aromatics but those present are heavy polycyclics which absorb so strongly in the UV that even small amounts are visible (at R_F 0.3) in Figure 60. In Figure 61 the major spot (R_F 0.7-0.8) is due to naphthenes and branched paraffins, the most prevalent types in lube oils (Section I.1.4). The aromatics are too few to be visualized well by $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$. The highly refined white oil, F, shows one, intense spot at the solvent front, due to paraffins, naphthenes and some olefins which make up its entire composition.

A somewhat similar pattern is revealed with iodine vapor (Figure 62). Again crudes and residual fuels are shown as one long smear while distillate products show typical discrete zones. Note the series of spots near the origin in the lube oil, 62D. These are due to polar additives and may be used to identify lubricants as described in Subsection IV.7.1 and Section V.

The differences between crudes, heating oils and diesels is further illustrated in Figure 63. Here cyclohexane was added to the system. Again the No. 2 oil shows a preponderance of heavy aromatics relative to the diesel.

Thin-layer chromatograms for a variety of weathered ships' fuels are shown in Figure 64I and II. Also included, for comparison is crude oil 10-A-2. The Navy distillate fuel, marine gas oil and marine diesel are clearly marked as distillate fuels (spots B, D and E) though quite similar to each other. Navy Special (C) and bunker fuel (F) are clearly residual fuels with bunker the heavier of the two. The outboard motor oil, G, looks like a typical lube oil, although less aromatic even than 50-A-1 (compare Figures 60 and 61).

IV.7.2 Effects of Weathering on TLC

Weathering has only minor effects on the characteristic TLC patterns of various oils and generalizations made on unweathered samples appear to hold for weathered materials as well. This is illustrated by Figures 65-67. Figure 65 shows samples of a No. 2 heating oil weathered for different periods. The basic pattern is preserved although there appears to be a slight build-up of the major spot of lower R_F value. This spot, we feel, represents heavy aromatics which would be expected to increase on weathering. The spots near the origin increase considerably in intensity also. These are apparently polar materials ascribable to either oxidation products or heavy additives and it is not surprising to see an increase in such materials.

In Figures 66 and 67, several different weathered oils are compared with unweathered samples. In all cases the basic TLC patterns remain unchanged over the 2 week period.

IV.7.3 Use of TLC in Identification of Oil Spills

Although primarily a classification tool, TLC may, in certain instances be useful in identifying oil samples as well. Oils within broad classes seem to give characteristic patterns such that, by comparison with an authentic sample, identification can be made. Four different No. 6 oils, all weathered two weeks were chosen at random and chromatographed on silica gel thin-layers with n-hexane: acetic acid (50:1) as the developing solvent. Results are shown in Figure 68. All oils show distinct patterns. The sample in Figure 68A (32-A-1-III) is more naphthenic and/or paraffinic than the others while B (32-A-2-III) has more heavy aromatics and fewer paraffins or olefins. The oils C and D (32-F-1-III and 32-F-2-III respectively) show distinct spots rather than a smooth continuum. Sample C has strong spots in the medium aromatic region and a relatively weak spot at the solvent front. The opposite is true for sample D. These results can no doubt be improved by optimizing the system.

Two other examples of TLC as an identification tool are afforded by Figures 69 and 70. These both take advantage of different polar materials, probably additives, occurring in these products. Figure 69 shows the behavior of two different No. 2 oils. Although the main pattern of spots ($R_F = 0.50 - 0.75$) is very similar, the spots near the origin ($R_F = 0-0.10$) are different. These are probably due to polar additives and will vary from product to product.

A particularly useful application of TLC to identification occurs in the case of automotive lube oils. As discussed in Section I, these materials have large amounts of additives, the amounts and types of which vary from lube to lube and manufacturer to manufacturer. These additives, being polar in nature, remain near the origin in the TLC systems we use and are well separated from the other components of the lube oils. By increasing the polarity of the eluting solvent somewhat (adding more acetic acid) these compounds can be separated into patterns characteristic of the lubricant in question. This is illustrated in Figure 70 where seven different lube oils, all weathered one week, are chromatographed on silica gel with an eluting solvent system of n-hexane: acetic acid (35:1). Surprisingly, these additives are best visualized with iodine vapors. All seven lubes have distinct patterns of spots with R_F 's ranging from 0-0.30. When tried on a blind basis, all seven were easily identified. Although these patterns are not dramatically altered by weathering (Figure 71), It is best, as in all cases of identification, to have an artificially weathered authentic sample. Additional examples of the use of TLC in lube oil identification are given in Section V.



Figure 59. Unweathered Oils Chromatographed on Silica Gel 60F plates, eluted with n-hexane: acetic acid (40:1) and visualized with short wave UV light (2500Å). A. Crude Oil, 10-A-1; B. No. 2 heating oil, 40-A-1; C. Automotive Diesel, 42-A-2; D. Lube Oil, 50-A-1; E. Bunker "C"; F. White Oil, 60-X-2; G. Crude Oil, 10-A-2.



Figure 60. Weathered Oils visualized with UV Light. Silica gel 60 F plates (0.2 mm), solvent: n-Hexane-Glacial Acetic Acid (50:1); Visualized with short wave (2500Å) light. A. Crude 10-A-1; B. No. 2 Heating Oil, 40-A-1; C. Automotive Diesel, 42-A-1; D. Multi-grade Lube Oil, 50-A-1; E. No. 6 Oil, 32-H-1; F. White Oil, 60-X-2; G. No. 5 Oil, 31-F-2; H. No. 4 Oil, 30-A-1.

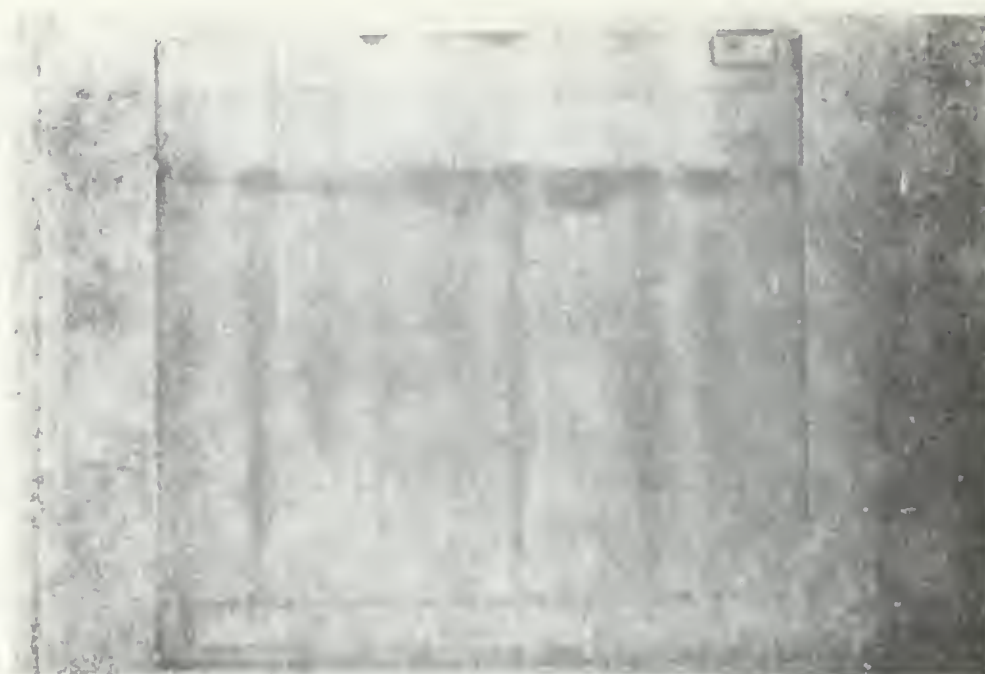


Figure 61. visualization with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$. Chromatographed as in Figure 60. A. Crude Oil; B. No. 2 Heating Oil; C. Diesel Fuel; D. Lube Oil; E. No. 6 Oil; F. White Oil; G. No. 5 Oil; H. No. 4 Oil. (All Weathered)



Figure 62. Visualized with iodine vapor. Chromatographed as in Figure 60. A. Crude Oil; B. No. 2 Oil; C. Diesel Oil; D. Lube Oil; E. No. 6 Oil; F. White Oil; G. No. 5 Oil; H. No. 4 Oil. (All Weathered)

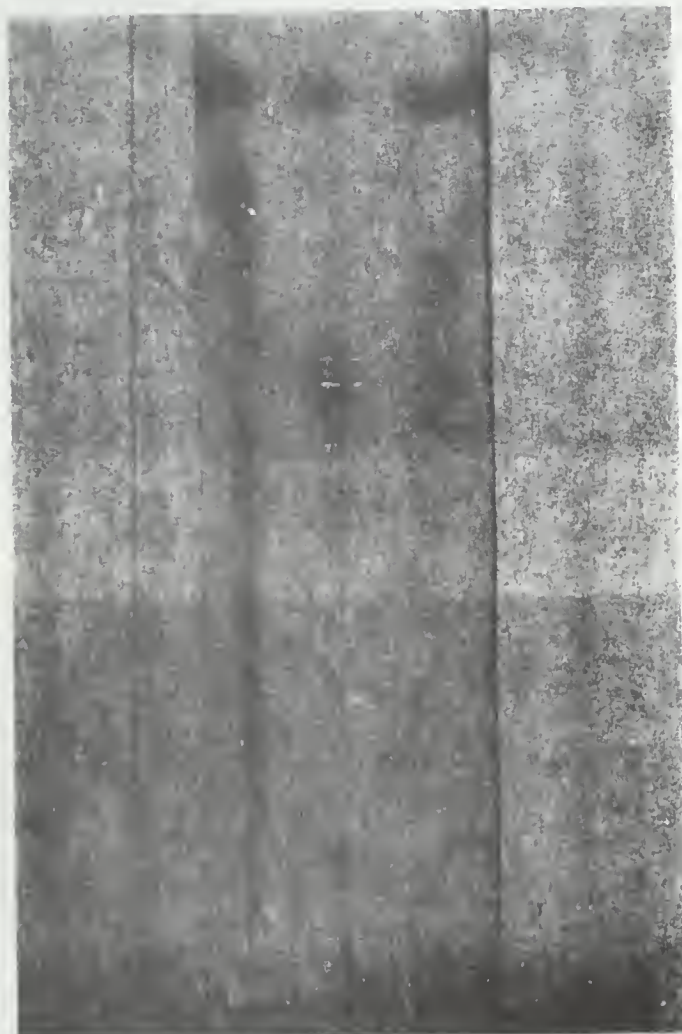
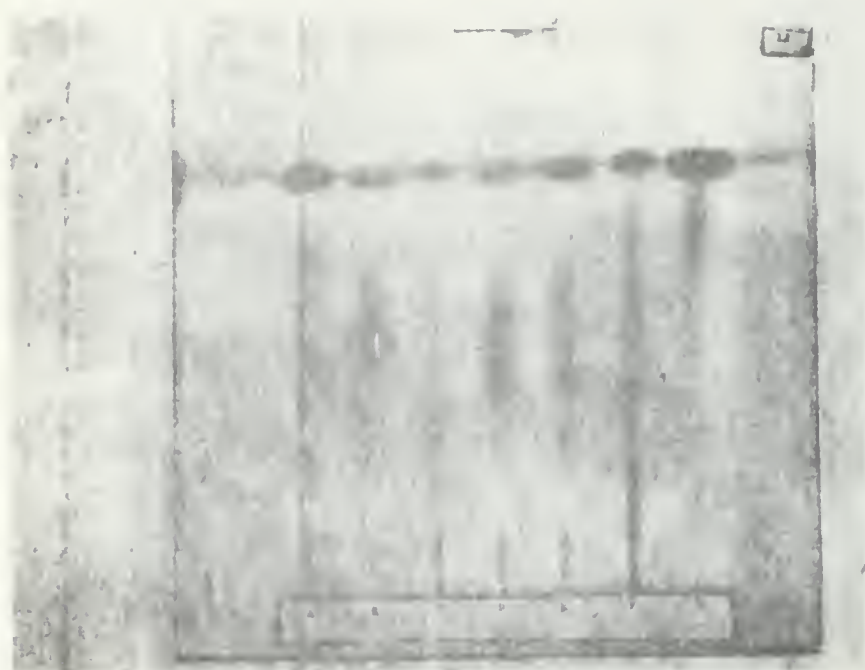


Figure 63. Thin-layer Chromatogram of Three Unweathered Oils, Visualized with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$. Silica gel 60F plates (0.2mm) eluted with cyclohexane: n-hexane: acetic acid (4:1:trace). A. Crude Oil 10-A-1; B. No. 2 Heating Oil, 10-A-1; C. Diesel Oil, 42-A-1.

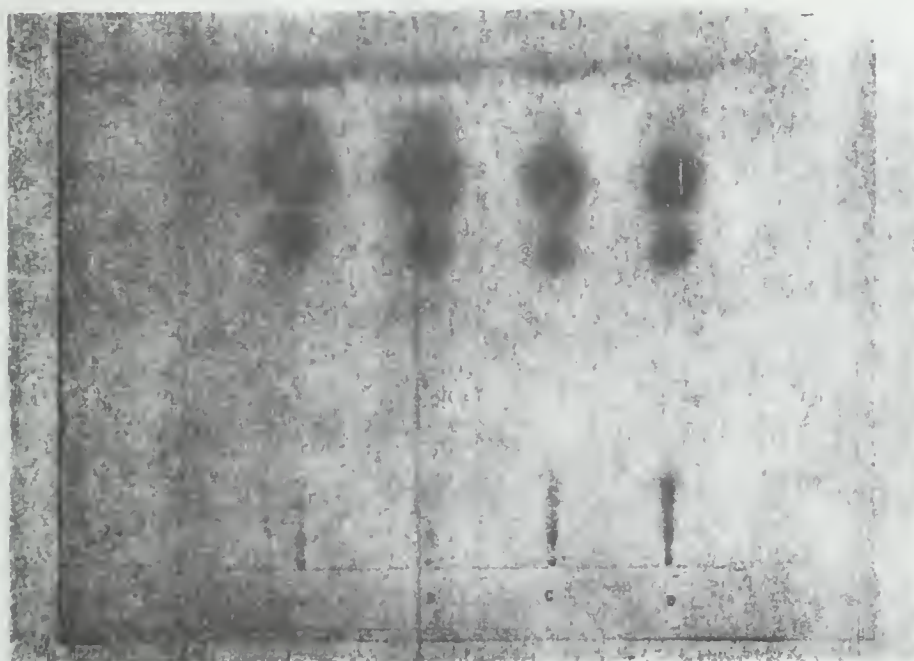


I. Visualized with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$

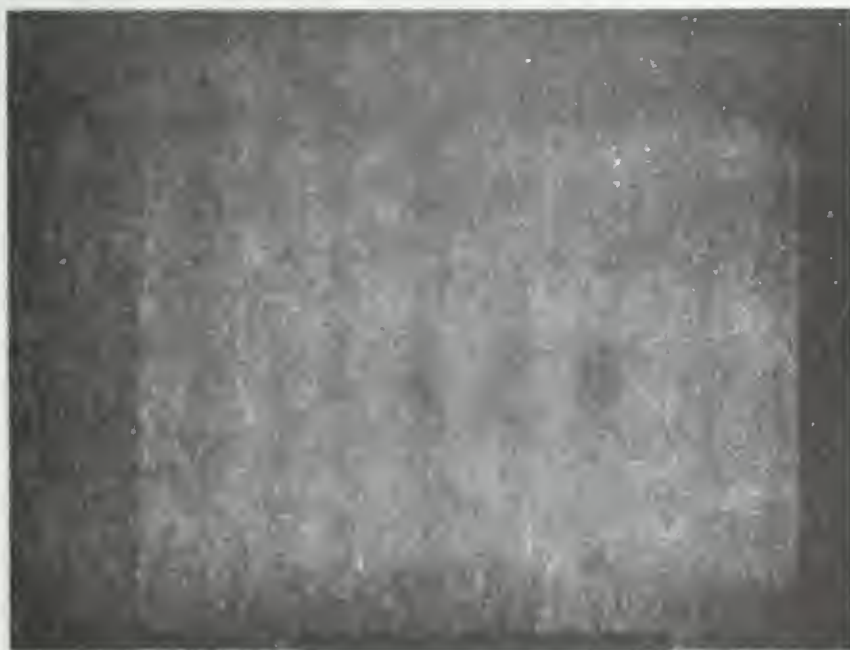


II. Visualized with UV Light

Figure 64. Thin-Layer Chromatograms of Some Ships' Fuels. Conditions as in Figure 60. A. Crude Oil 10-A-2; B. Navy Distillate Fuel, 45-X-1; C. Navy Special, 33-X-1; D. Marine Gas Oil, 41-A-1; E. Marine Diesel, 42-A-3; F. Bunker Fuel, 20-A-1; G. Outboard Motor Oil, 60-X-3.



I. Visualized with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$



II. Visualized with UV Light.

Figure 65. Effect of Weathering on Thin-Layer Chromatograms of No. 2 Heating Oil, 40-A-1. A. Unweathered; B. Weathered One Day; C. Weathered One Week; D. Weathered Two Weeks. Conditions as in Figure 60.

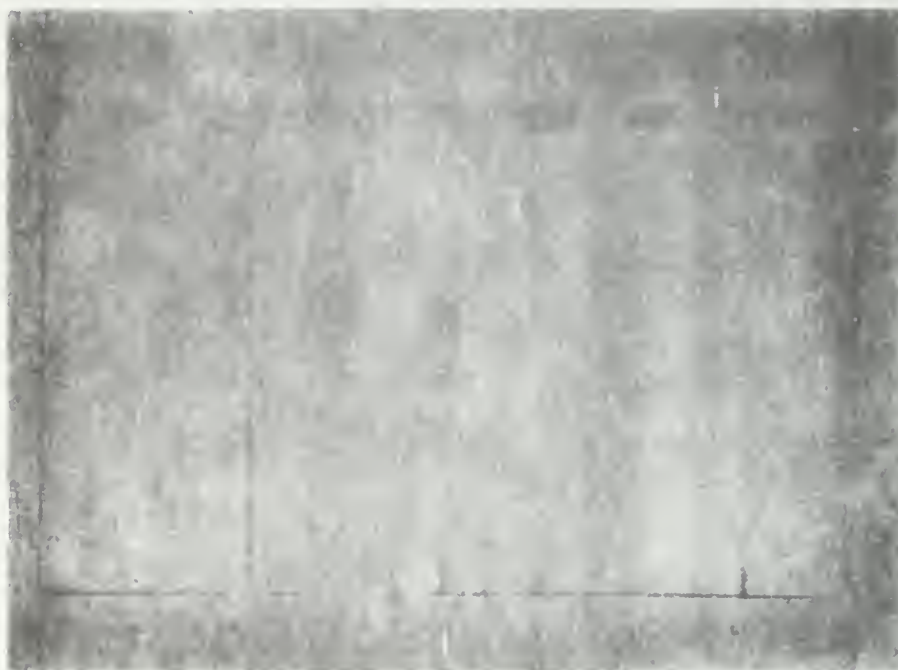


Figure 66. Effects of Weathering on TLC of Test Oils. Conditions as in Figure 60 Visualized with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$ (Charring). A. Diesel Oil unweathered; B. Weathered two weeks; C. No. 2 Oil unweathered; D. Weathered two weeks; E. Lube Oil unweathered; F. Weathered two weeks; G. Crude Oil weathered two weeks.



Figure 67. Effects of Weathering as Visualized by UV Light Condition as in Figure 60. A. No. 2 Oil unweathered; B. Weathered two weeks; C. Diesel Oil unweathered; D. Weathered two weeks; E. Lube Oil unweathered; F. Weathered two weeks.



Figure 68. Thin-Layer Chromatogram of Four Weathered No. 6 Oils.

System: Silica gel 60F (0.2 mm) developed with *n*-hexane:
acetic acid (50:1); visualized with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$ (charring).
A. 32-A-1-III; B. 32-A-2-III; C. 32-F-1-III; D. 32-F-2-III.



Figure 69. Thin Layer Chromatogram of Two No. 2 Oils.

Conditions as in Figure 68; visualized with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$
A. 40-A-1-0. B. 40-A-2-0



Figure 70. Additive Patterns in TLC of Various Weathered Lube Oils.

Conditions: Silica gel 60F (0.2 mm) developed with n-hexane:
acetic acid (35:1) visualized with iodine vapor. A. 50-C-1;
B. 50-G-2; C. 50-D-1; D. 50-A-1; E. 50-C-2; F. 50-A-2;
G. 50-F-2.

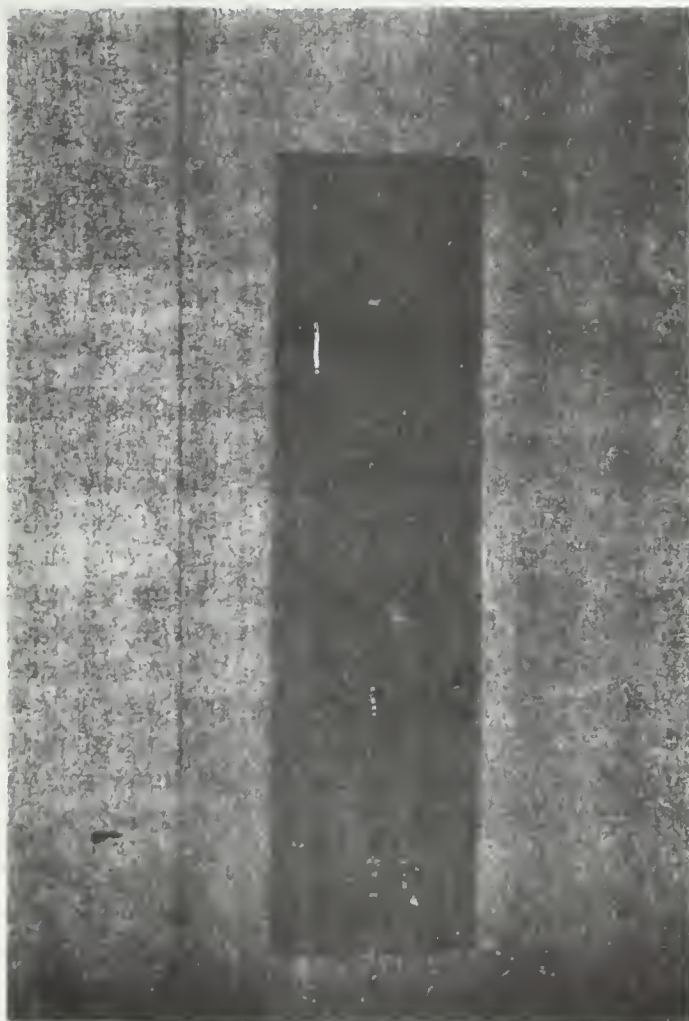


Figure 71. Effect of Weathering on TLC Patterns of Lube Oils 50-G-1.

Conditions as in Figure 70. A. Unweathered; B. Weathered one week; C. Weathered two weeks.

IV.8 Liquid-Liquid Chromatography

Liquid-liquid chromatography (liquid chromatography or "LC" for short) has only recently been applied to the problem of characterizing petroleum products (24,34). Our preliminary results suggest that this technique can be developed into a powerful tool for both classifying and identifying spilled oil. The work described in this section should be regarded as a feasibility study aimed at determining the potential of the method and its limitations. This research was not part of the original proposal but was substituted for part of the specific gravity-GC distillation analyses as discussed in Section III. The advantage of the LC method lies in its speed and simplicity. Interpretation is straightforward. Analysis time is less than 20 minutes, and a sample size of 1 μ l suffices. Samples can generally be injected neat. For dilution and extraction purposes, carrier liquids can be used, in which case no interference from the solvent occurs. Extraneous polar organic substances (detergents, bio-organic materials, etc.) are generally absorbed by the column and do not interfere. The ability of LC to separate heavy PNA components from lighter components and to visualize them at low concentrations appears to be particularly useful in this application because the chromatogram of the heavier components is expected to be little affected by weathering. One disadvantage of LC, at the present state of art, is that column resolution cannot be made to order. Different laboratories will obtain somewhat different fingerprints. Even within the same laboratory column activity can change resulting in fingerprint variations. One can therefore not resort to a reference library of fingerprints. It is necessary to run reference products and samples from suspected oil spill sources in parallel to the unknown sample. A second problem, the effects of weathering, must be taken into account as well. Simple ways to obviate these difficulties are discussed in Subsection IV.8.4. below.

Several different detectors can be used for LC work. In the present investigation, we used both ultraviolet (UV) and refractive index (RI) detectors in series and obtained two separate chromatograms for each sample put through the column. The first of these records the presence of UV-absorbing (generally aromatic) components, while the Refractive Index (RI) detector records the total sample, including paraffins and olefins. The UV chromatograms are better resolved and, generally, more useful. A typical chromatogram is shown in Figure 72. A standard blend of hydrocarbons was used and the peaks are identified. If an unknown sample is chromatographed under the same conditions (preferably directly before or after the standard) the same types can be detected.

IV.8.1 Use of LC in the Classification of Petroleum Products

The liquid chromatograms for several different unweathered petroleum products are shown in Figures 73-77*. For this application, LC is much like TLC in that it can readily distinguish crudes and heavy fuels as a class from refined products such as distillate fuels, white oils, lube

- - - - -
* Note that, in these figures, a non-routine type of alignment was used so that the injection points and corresponding peaks of the RI and UV trace coincide. They are usually offset as in Figure 72.

It would be difficult, however, to distinguish a weathered crude from a heavy fuel, a No. 2 oil from a diesel or one heavy fuel from another without an authentic sample.

For example, the two unweathered crudes, Figures 73 and 74 have broad peaks which tail considerably at long retention times, in both the RI and UV chromatograms rather than the compressed traces for the distillate fuels (Figures 75 and 76). The two distillate fuels, while clearly different, could not be classified as diesel and No. 2 without an authentic sample. The chromatogram of a No. 6 oil, 32-F-1, is shown in Figure 77. It is clearly identified as a residual fuel or a weathered crude by its broad eluting range and preponderance of heavy ends. However, this trace was run at a different date than those in Figures 72-76. As a result, the peaks are not superimposable. This points up the need to run authentic samples as soon as possible after the pollution sample if other than rough classification is needed.

IV.8.2 Identification Using Liquid Chromatography

Because of its higher resolution, LC may be more generally useful as an identification technique than TLC*. For example the two crude oils shown in Figures 73 and 74 have clearly distinct patterns and relative peak heights in both the RI and UV chromatograms. A further example is afforded by Figures 78 and 79. Here LC's for two heavily weathered No. 6 oils are contrasted. The patterns and relative peak height are quite different. It appears that liquid chromatography has considerable promise as part of a classification-identification system. Additional examples are given in Section V. However, some additional development and optimization will be required. Two of the problems were mentioned above; columns change with respect to resolution and retention times because of varying degrees of activation, and the effects of weathering cannot be predicted. The first of these difficulties is easily obviated by keeping columns properly conditioned and, more importantly, by analyzing "known" and unknown samples close together. The effects of weathering and how they can be overcome is discussed in the following subsections.

IV.8.3 Effects of Weathering on Liquid Chromatograms

Liquid chromatograms for some weathered and unweathered oils are shown in Figures 79-82. In the case of the heavy No. 6 oil (Figure 79 vs 80) the differences are not great and the weathered sample (32-H-1-III, Figure 79) is clearly the same as the unweathered oil (Figure 80). The situation with the lighter No. 2 oil (Figures 81 and 82) is quite different. Here the trace for the weathered sample (Figure 82) is so altered that it is unrecognizable as being derived from the unweathered oil (Figure 81**). It is apparent that an identification could not be made on the basis of these two trials.

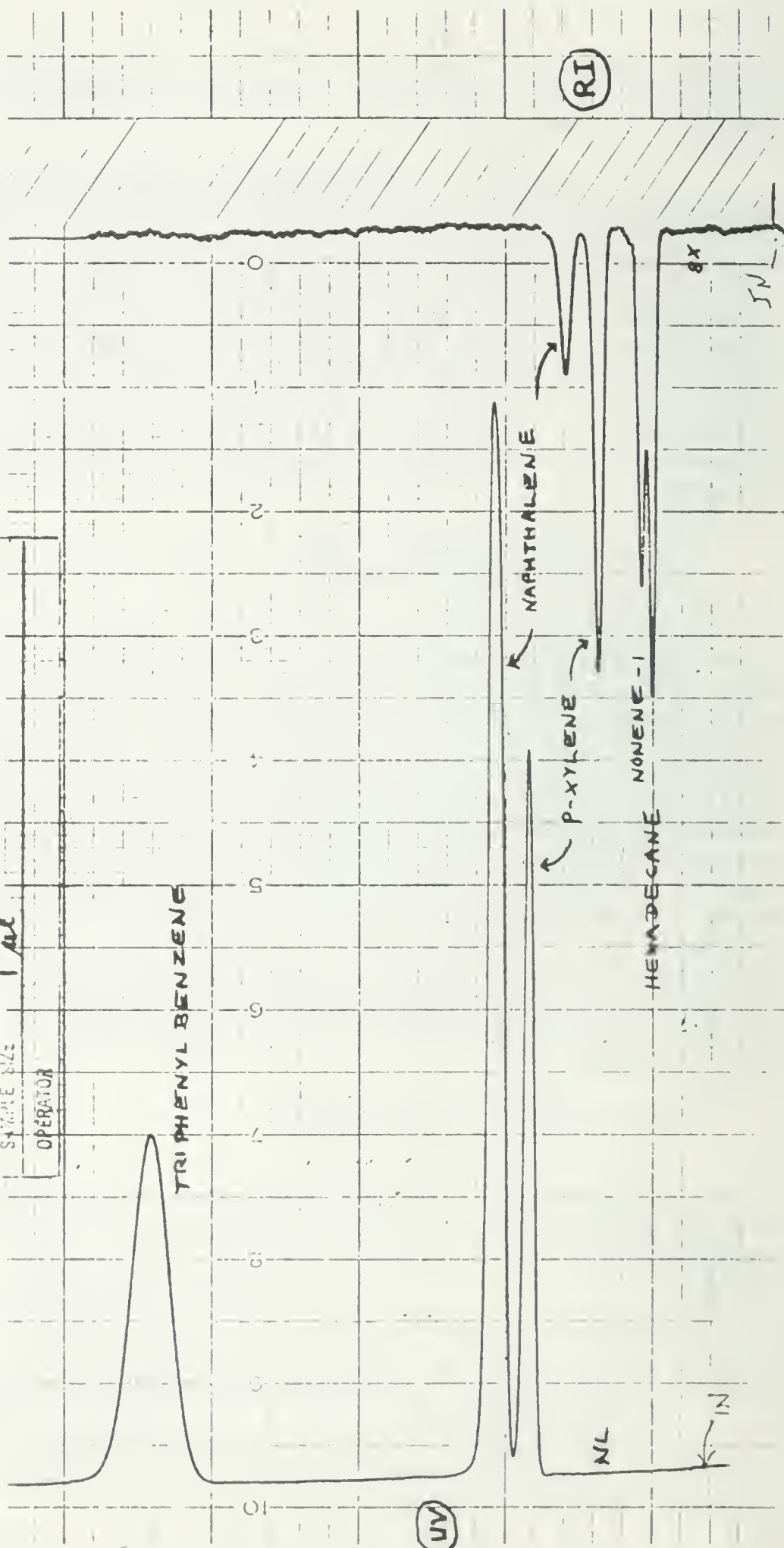
- - - -
* It should be emphasized that the two are complementary, not equivalent. Thus, the unique application of TLC in identifying lube oils can be accomplished only with difficulty by LC.

** Note that Figures 75 and 81 are the same sample chromatographed at different times. The second time (Figure 81) a more active column was used and somewhat better resolution was achieved.

Figure 72

Liquid Chromatogram for
Standard Blend of
Hydrocarbon Types

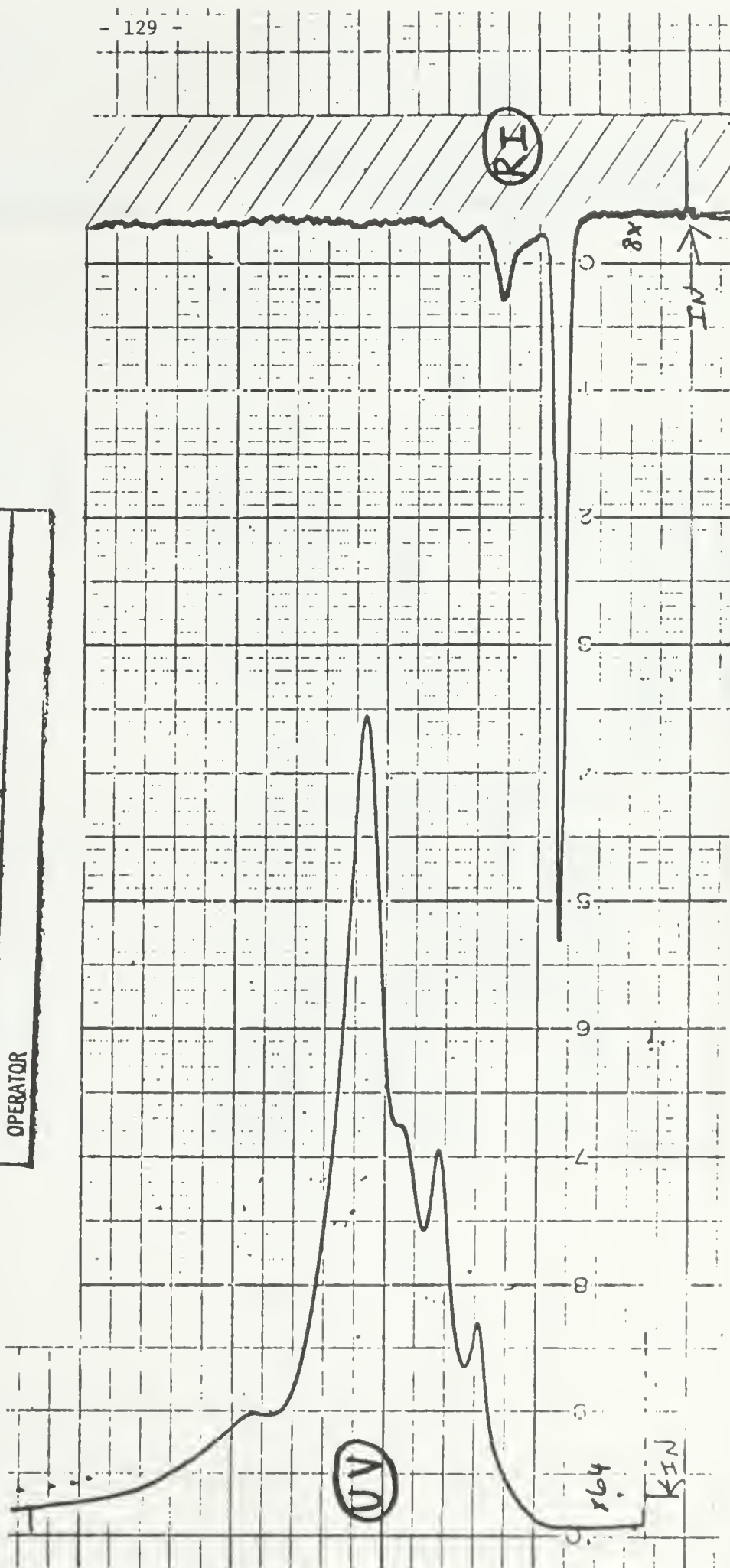
LIQUID CHROMATOGRAPHY			
A. L. No.	STD. BLEND OF HYDROCARBON TYPES		
NAME	W. SCHULZ		
DATE	10/18/73		
COUNT	4 ft. TORASIL A+T		
LEAD	4 ft.	TYPE	
PRESSURE	1000 PSI	CHART SPEED	0.2
FLOW RATE	1.0 ML/MIN. ISOCTANE		
TEMP. PROG.	%/°C	HOLD	
SPD.	0.01	ATTENUATION	
SAMPLE SIZE	1 µl		
OPERATOR			



LIQUID CHROMATOGRAPHY

XL No.	337049
SAMPLE	CRUDE OIL
NAME	FRANKENFELD SECTION
DATE	10/18/73
COLUMN	PARASIL A+T
LENGTH	4 ft.
PRESSURE	1000 PSI
CHART I.P.M.	0.2
FLOW RATE	1.0 MB/MIN
TEMP. PROG.	°C/MIN. HOLD
VOLTS	0.01
ATTENUATION	
SAMPLE SIZE	0.4 µL, 0.8 µL
OPERATOR	

Figure 73. Liquid Chromatogram for Crude Oil 10-A-2



LIQUID CHROMATOGRAPHY

A. L. 337057

SAMPLE

CRUDE OIL

10-A-3-0

NAME FRANKENFELD

DATE 10/18/73

RE NO.

COLUMN PORASIL A+T

LENGTH 4 ft.

TYPE

PRE PRESS 1000 PSI

COUNT RPM 0.2

FLOW RATE: 1.0 ML/MIN. ISOOCTANE

TEMP. PROB.

°C/MIN.

HOLD

VOLTS 0.01

ATTENUATION

SCALE 0.4 ml, 0.8 ml

OPERATOR

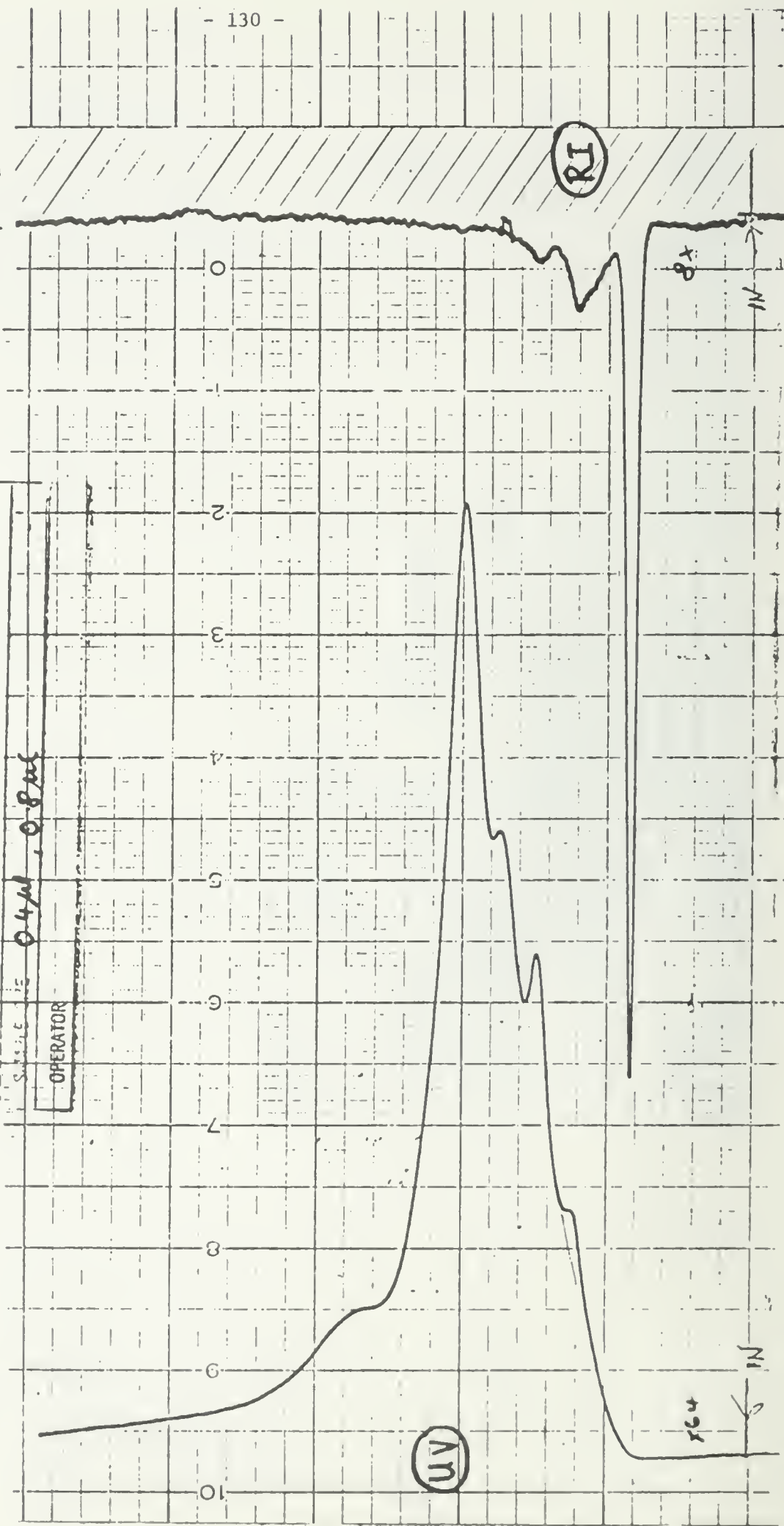


Figure 74. Liquid Chromatogram for Crude Oil 10-A-3

Figure 75. Liquid Chromatogram of No. 2 Oil 40-A-1 (Both UV and RI Detection)

LIQUID CHROMATOGRAPHY	
A. L. No.	337041
SAMPLE	#2 HEATING OIL
	40-A-1-O
NAME	FRANKENFELD SECTION
DATE	10/18/73
CHARGE NO.	
COLUMN	POASIL A+T
LENGTH	4 ft.
TYPE	
PRESSURE	1000 PSI
CHART I.P.M.	0.2
FLOW RATE	1.0 ml/min
ISOOCTANE	
TEMP. PROG.	°C/min.
HOLD	
VOLTS	0.01
ATTENUATION	
SAMPLE SIZE	0.1 µl
	0.8 µl
OPERATOR	

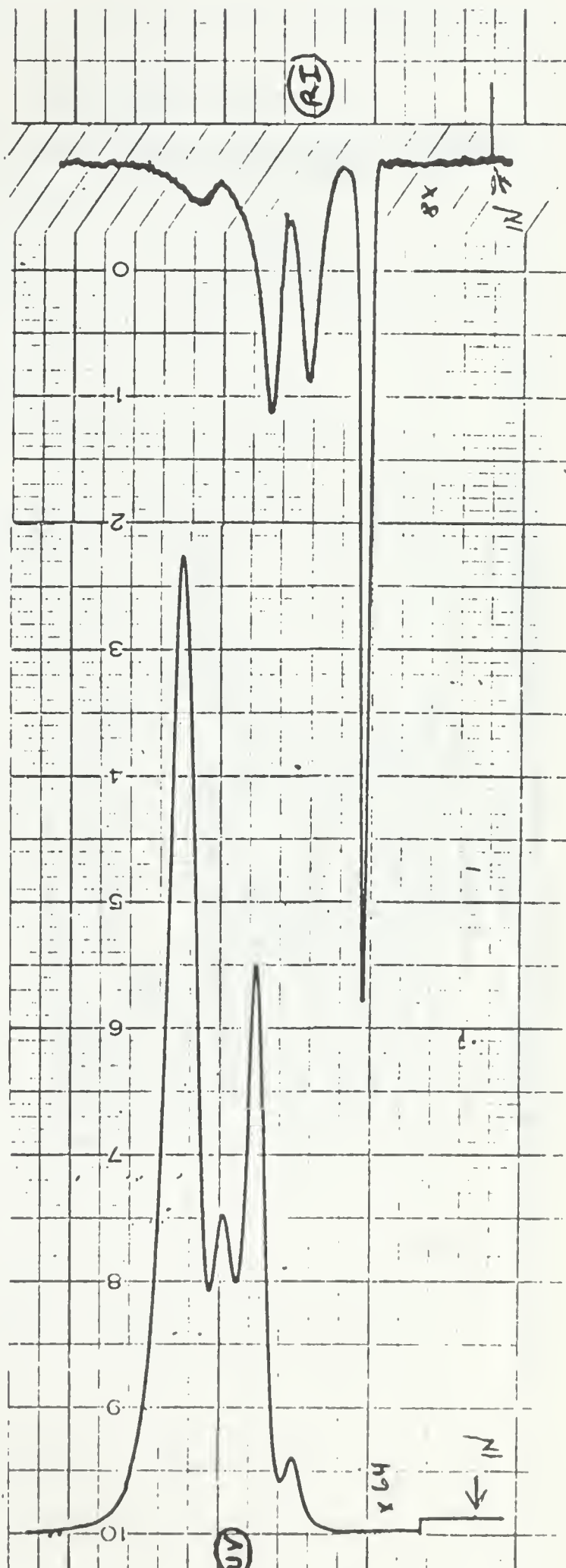


Figure 76. Liquid Chromatogram of Diesel Oil 42-A-1

LIQUID CHROMATOGRAPHY			
A. L. No.	337027		
SAM. L.	DIESEL OIL		
NAME	FRANKENFELD SECTION		
DATE	10/18/73	CHARGE NO.	42-A-1-0
COLUMN	PORASIL A+T	LENGTH	4 ft.
PRESSURE	1000 PSI	CHART I.P.M.	0.2
FLOW RATE: 1.0 ML/MIN. ISOOCTANE			
TEMP. PROG.	0.01	°C/MIN.	HOLD
SAMPLE SIZE	0.1 μ l, 0.8 μ l		
OPERATOR			

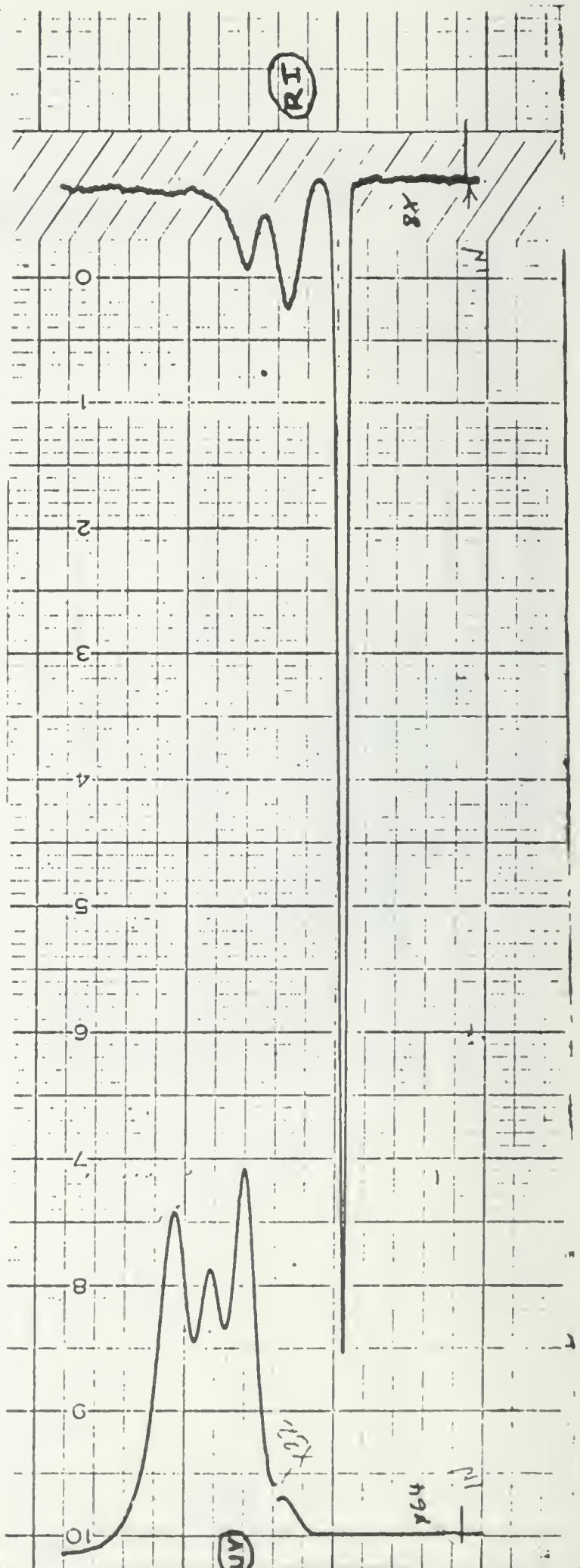


Figure 77. Liquid Chromatogram of No. 6
Oil 32-F-1-0

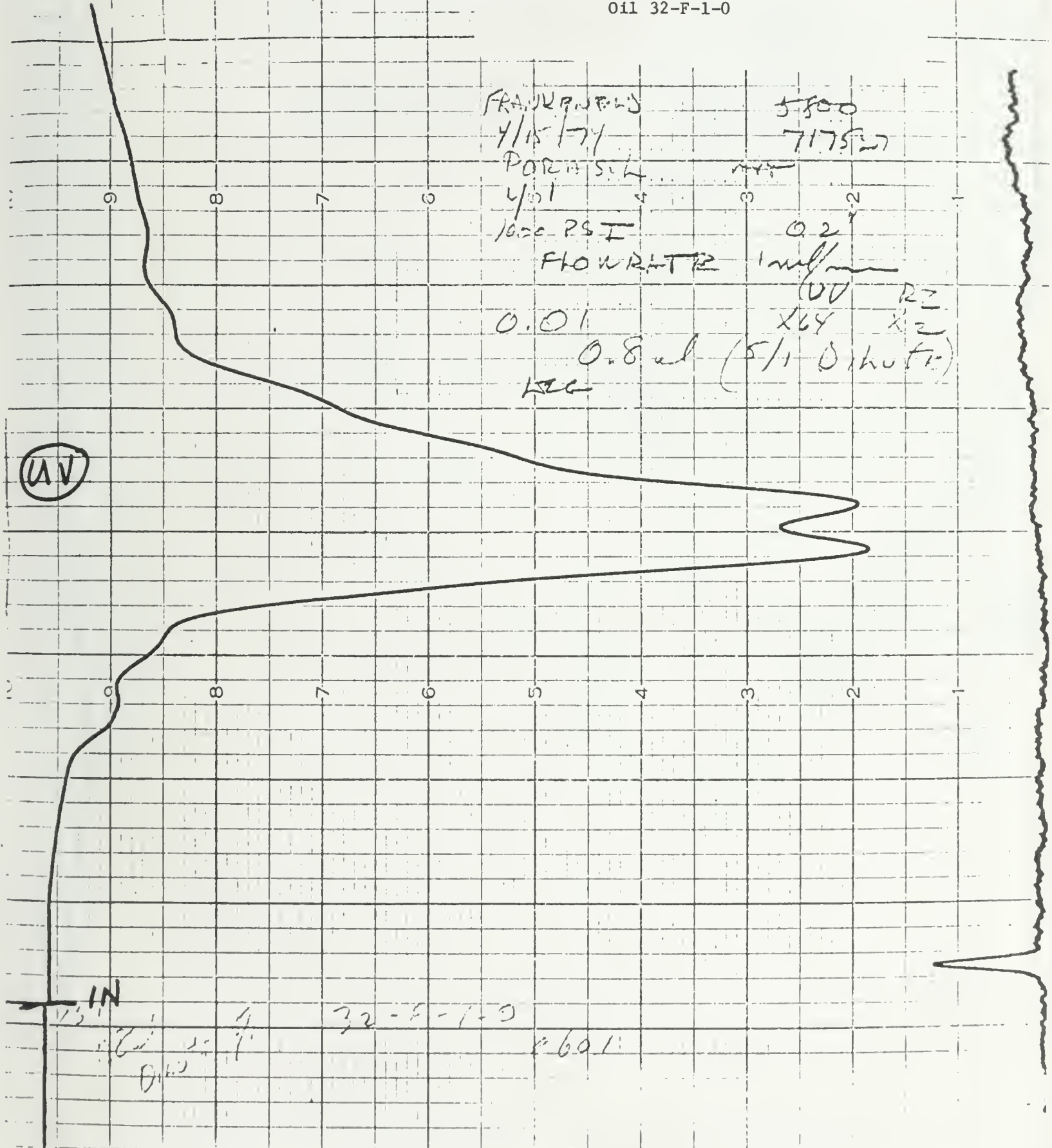


Figure 78. Liquid Chromatogram of
No. 6 Oil 32-F-1-III

FRANKENFELD

5800

4/10/77

7/7/527

Porapak Q

10-10

4"

1000 PSI

0.2"

Flow rate 1 ml/min

UV R_{max}

0.01

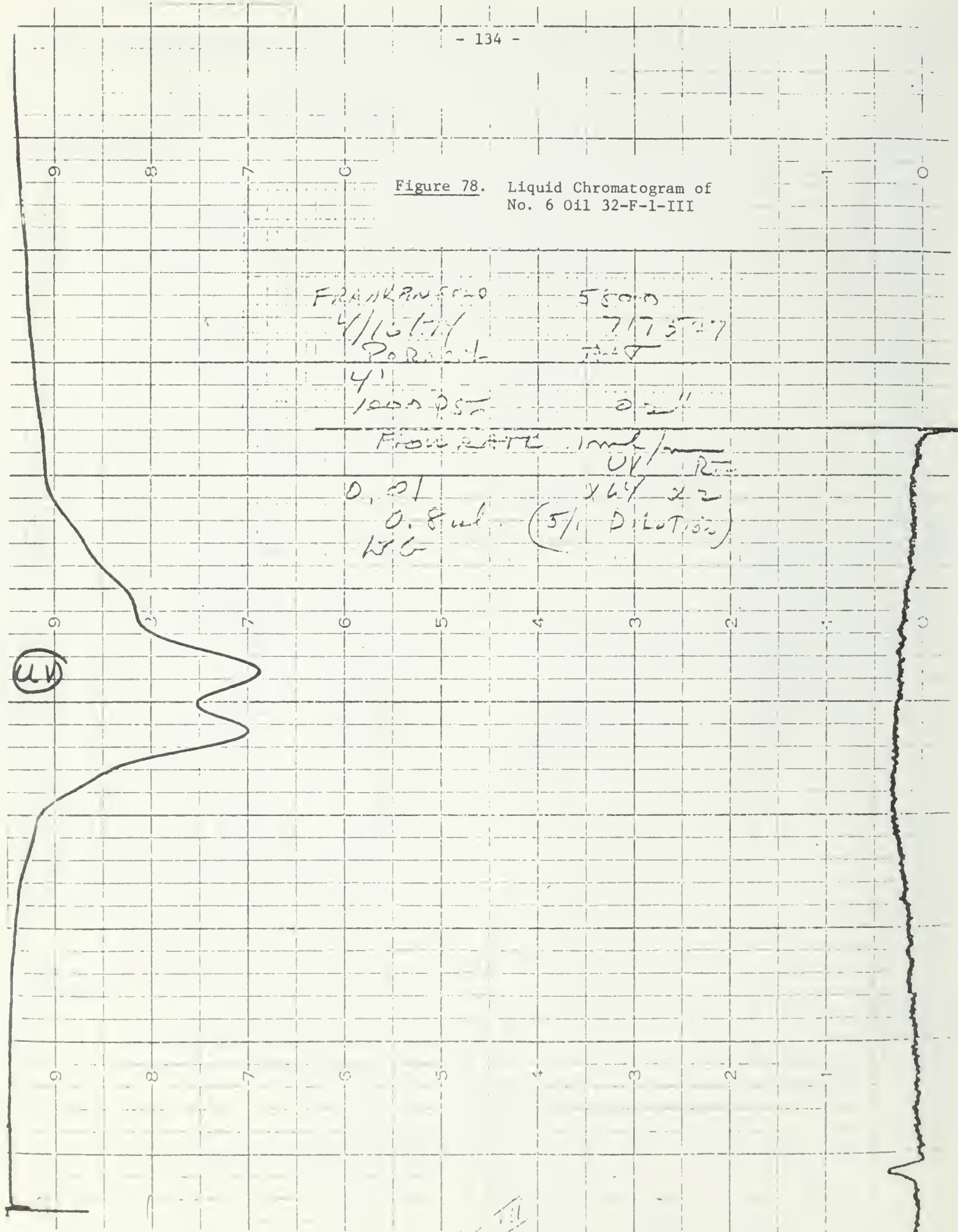
264 22

0.8 ul

(5/1 Dilution)

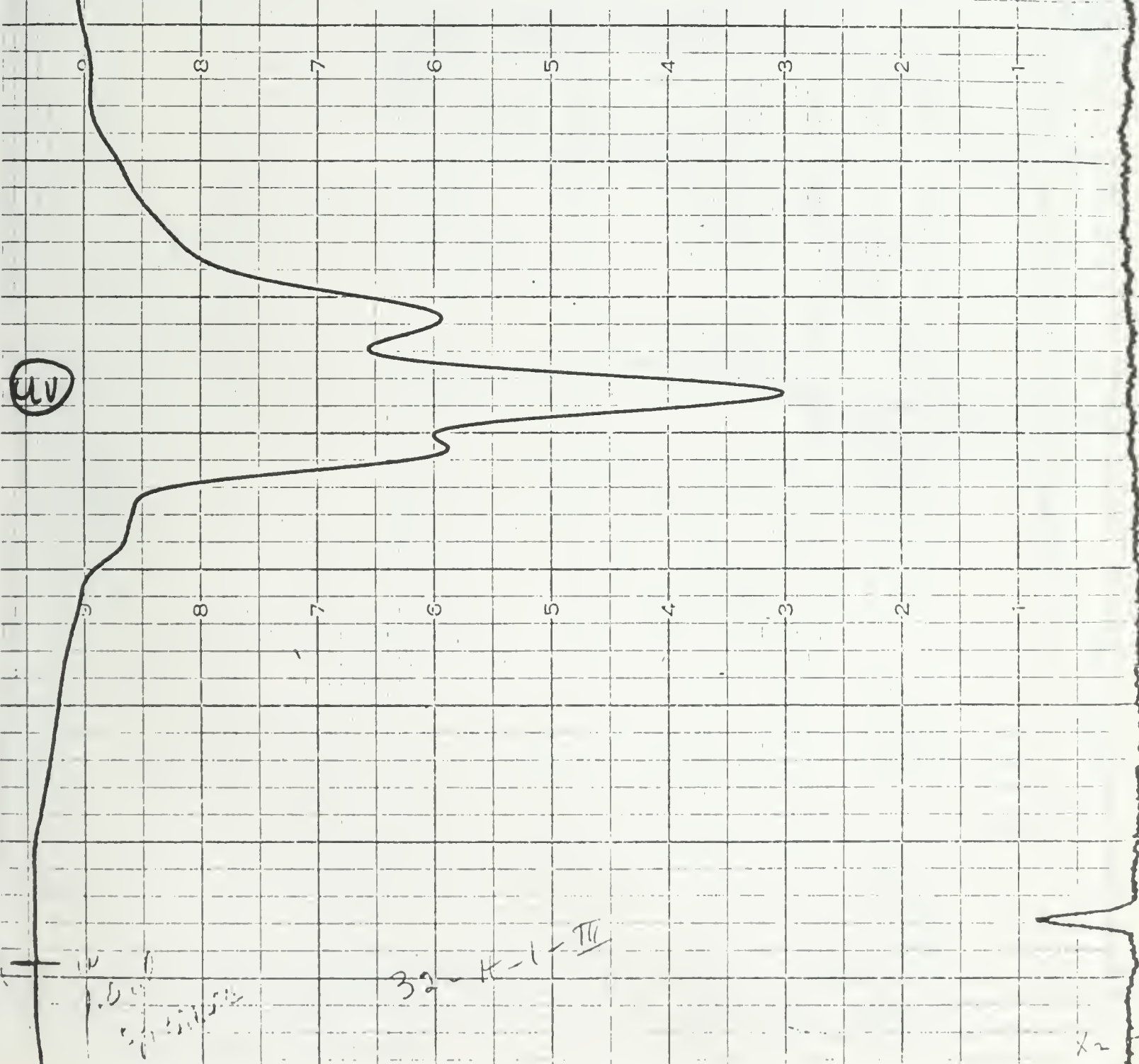
W.C.

(UV)



7/16/74 - 135 - 71752
 PARASIL AIR
 41
 100 PSI 0.2"
 FLOW RATE 1ml/min
 0.01 UV RI
 1.0 ml (5/1 Dilution) X2

Figure 79. Liquid Chromatogram for No. 6 Oil 32-H-1-III



32-H-1-III

Figure 80. Liquid Chromatogram for
No. 6 Oil 32-H-10

FRANKENFELD

4/16/74

PO 245.7

4"

1000 PSI

FLOW RATE 1 ml/min

0.01

0.8 ml

1.2 ml

5800

7175-7

RT

0.2"

UV

X04

(5/1 dilution)

P2

X2

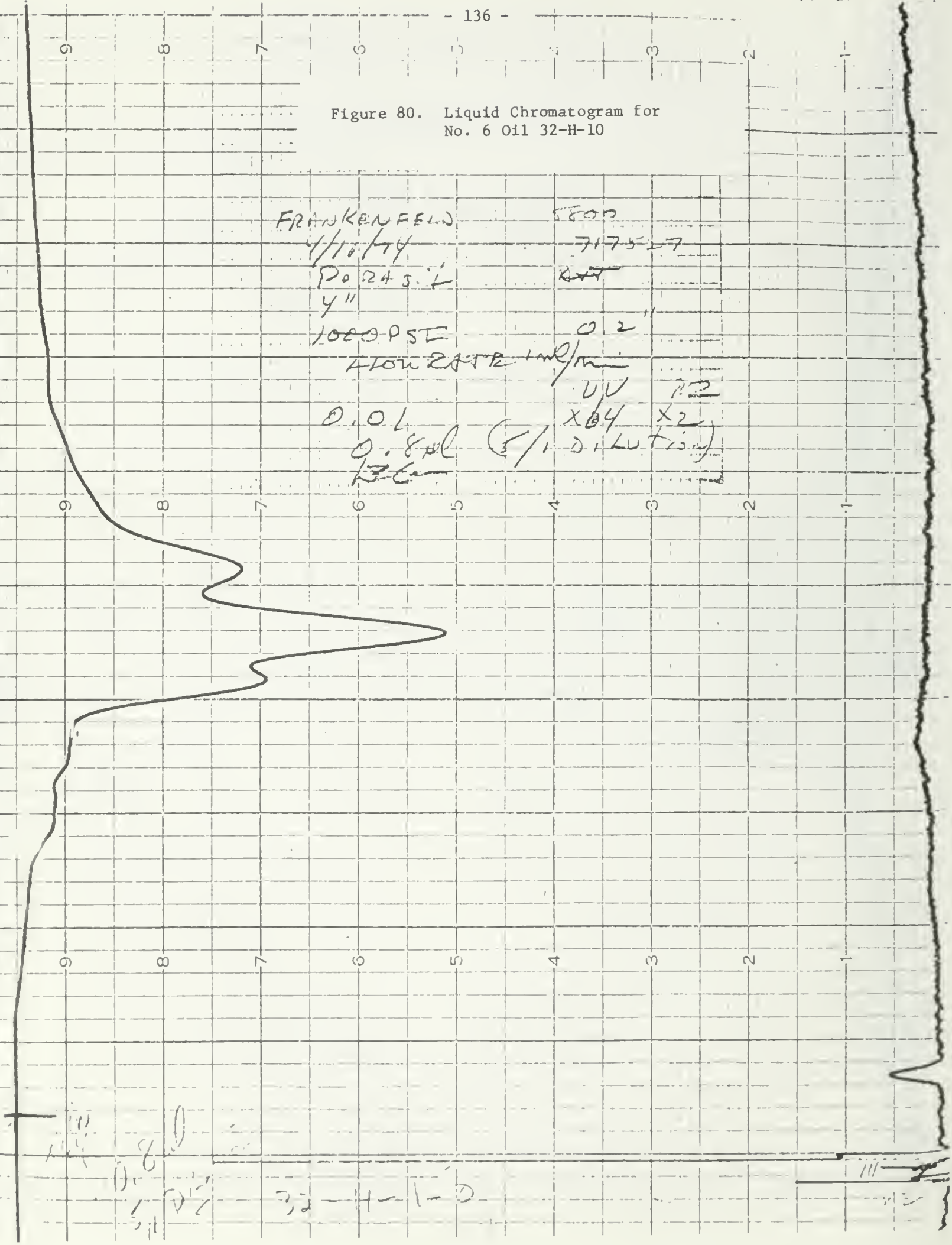
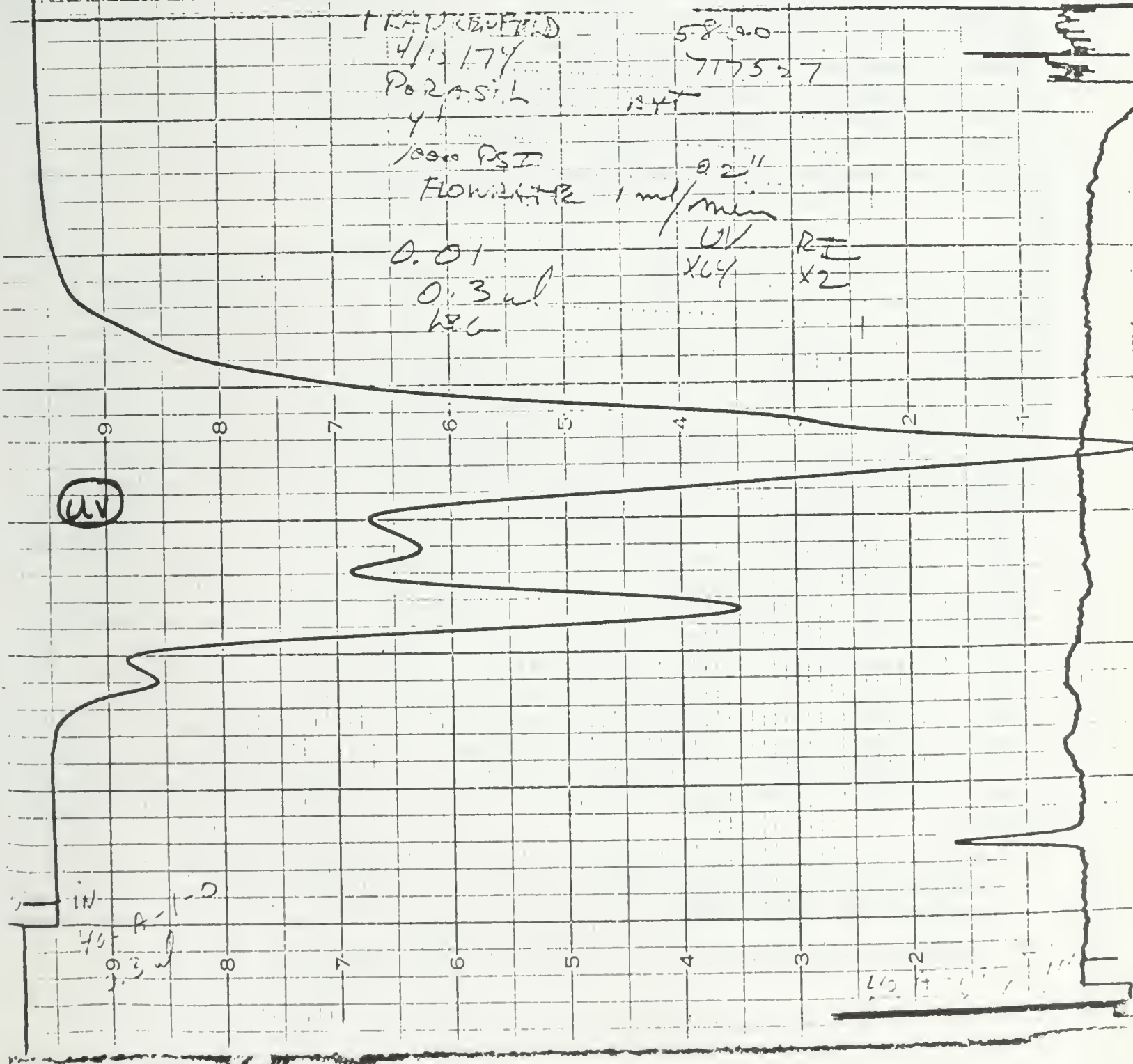


Figure 81. Liquid Chromatogram
of Unweathered No.
2 Oil 40-A-1-0



IV.8.4 Solving the Weathering Problem in Liquid Chromatography

Two methods for accounting for weathering effects have been investigated. Both are effective and the choice of which to employ would be largely a matter of convenience.

The first method entails artificial weathering of authentic samples. The best of several ways to do this is by using a steam jacketed buchner funnel, floating the oil on a layer of salt water and bubbling hot air through the mixture for about four hours (see Section III.2.2). In the case of the No. 2 heating oil studies, the "weathered" oil thus obtained compares favorably with a sample weathered for two weeks in a simulator whether analyzed by LC (compare Figures 82 and 83) or by gas chromatography (compare Figure 84 with 85B)*. The agreement is good enough to permit identification with a high degree of confidence. It is recommended that artificial weathering of some degree be employed with suspect samples regardless of which type of analytical procedure is used.

A second way to avoid the weathering problem, which actually serves as a separate analytical tool, is to separate and chromatograph only the heavy polynuclear aromatics (PNA's) that is, condensed aromatics having from 3 to 7 rings. PNA's are found in all petroleum products, even in oils as light as gasoline, and their patterns are not changed significantly on weathering. Different oils of all types have different relative amounts of 3, 4, 5 ring aromatics (1) and, if one could separate and analyze for them, this fraction would make up an effective fingerprint. Separation of the fraction can be accomplished in a variety of ways; trapping of late eluting components from liquid-liquid chromatograms (35); column chromatography on alumina (32) or clay gel (1) or, as we have used recently, extraction of the weathered or unweathered sample with nitromethane or acetonitrile (35). The isolated PNA fraction, after concentration of the sample is chromatographed by reversed phase (essentially partition) liquid chromatography on specially prepared columns of fine particles of silica gel coated with a monomolecular layer of n-octadecane**, eluted with acetonitrile. A typical chromatogram of some standard PNA's of from 4-6 condensed rings is shown in Figure 86. The peaks are identified on the figure. A similar trace for the acetonitrile extract of a weathered No. 2 heating oil (40-A-1-III) appears in Figure 87. The chromatograms show a series of well-resolved peaks in the 3-5 ring regions. Although not yet fully developed, this technique appears to have considerable promise to broadening the scope of the LC method.

- - - - -

* Note that the samples in Figure 85A and B are identical to those in Figures 48A and D respectively except that a slightly different column packing was used (2% SE-30 vs 3% SE-30).

** Columns obtained from Waters Associates Inc. Framingham, Mass.

Figure 82. Liquid Chromatogram of No. 2 Oil
40-A-1-III (weathered 3 weeks)

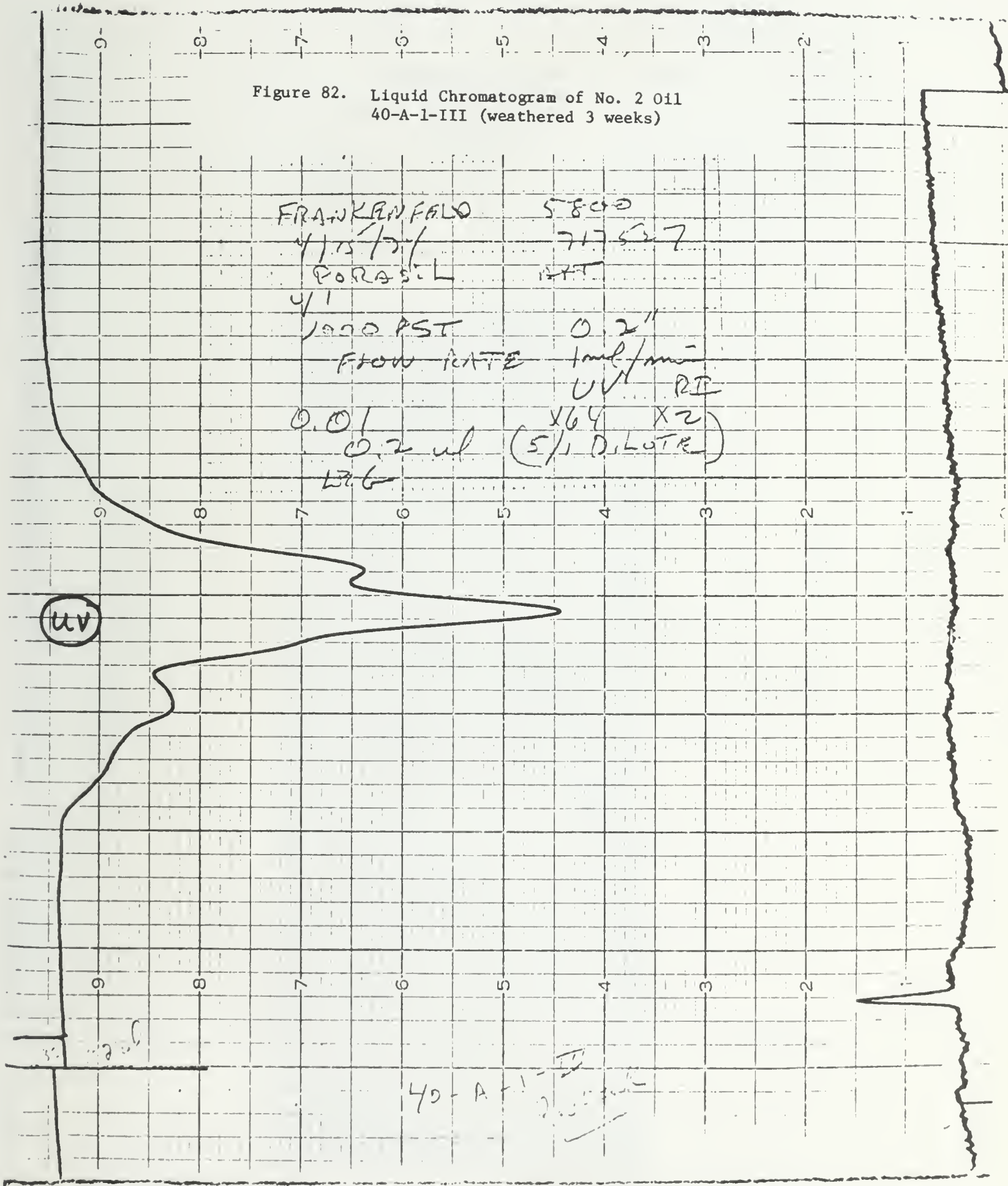


Figure 83. Liquid Chromatogram of
No. 2 Oil 40-A-1
Weathered Under Acceler-
ated Conditions

40-A-1-G 121.0. Buck 4hrs 4-17-77
(DILUTED 2% in isoctane)

1 ml/min isoctane

0.2/min

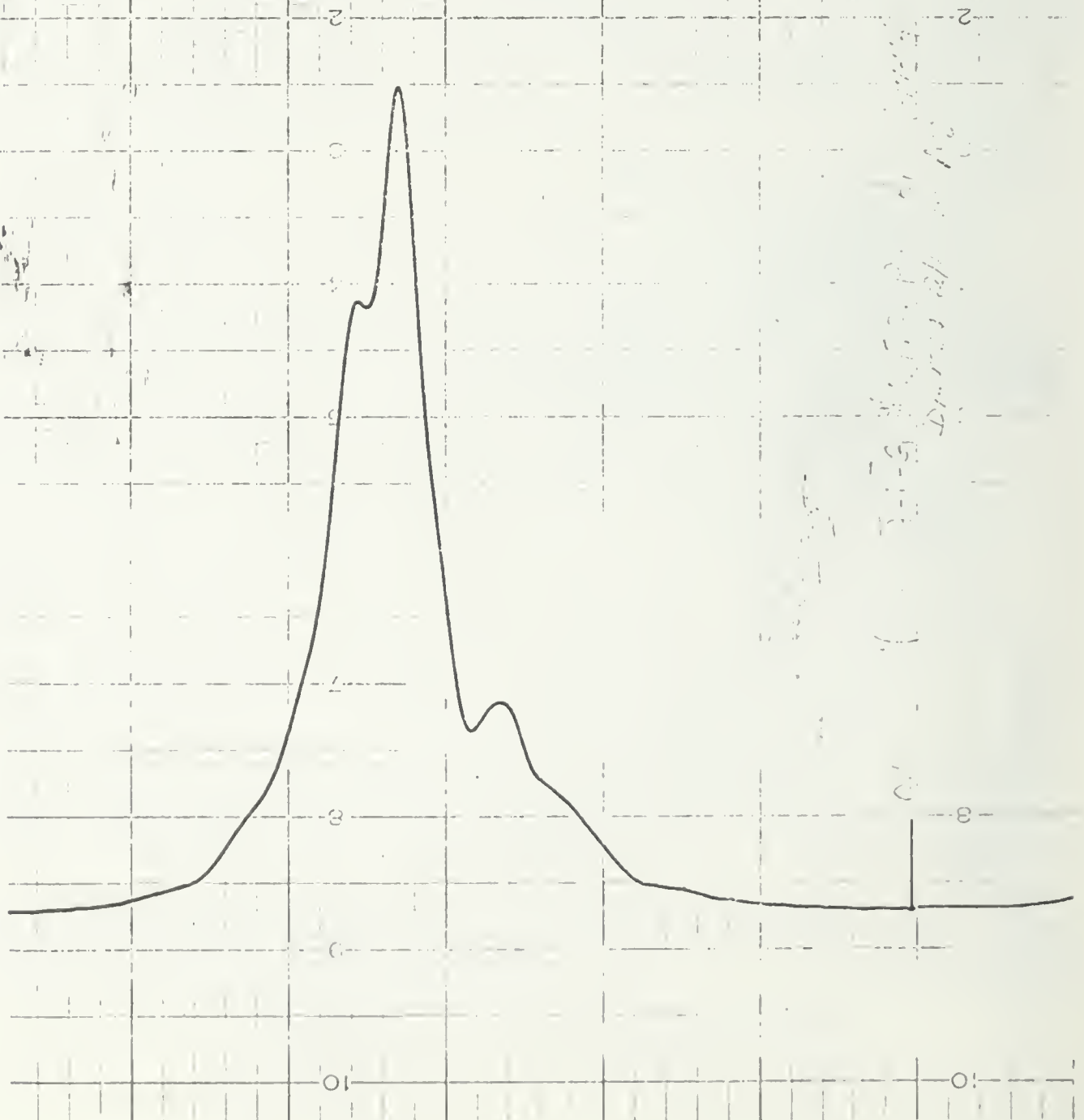


Figure 84. GC Fingerprint of No. 2 Heating Oil 40-A-1 Weathered 2 Weeks in Simulator

Column: 15', 1/8", 2% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

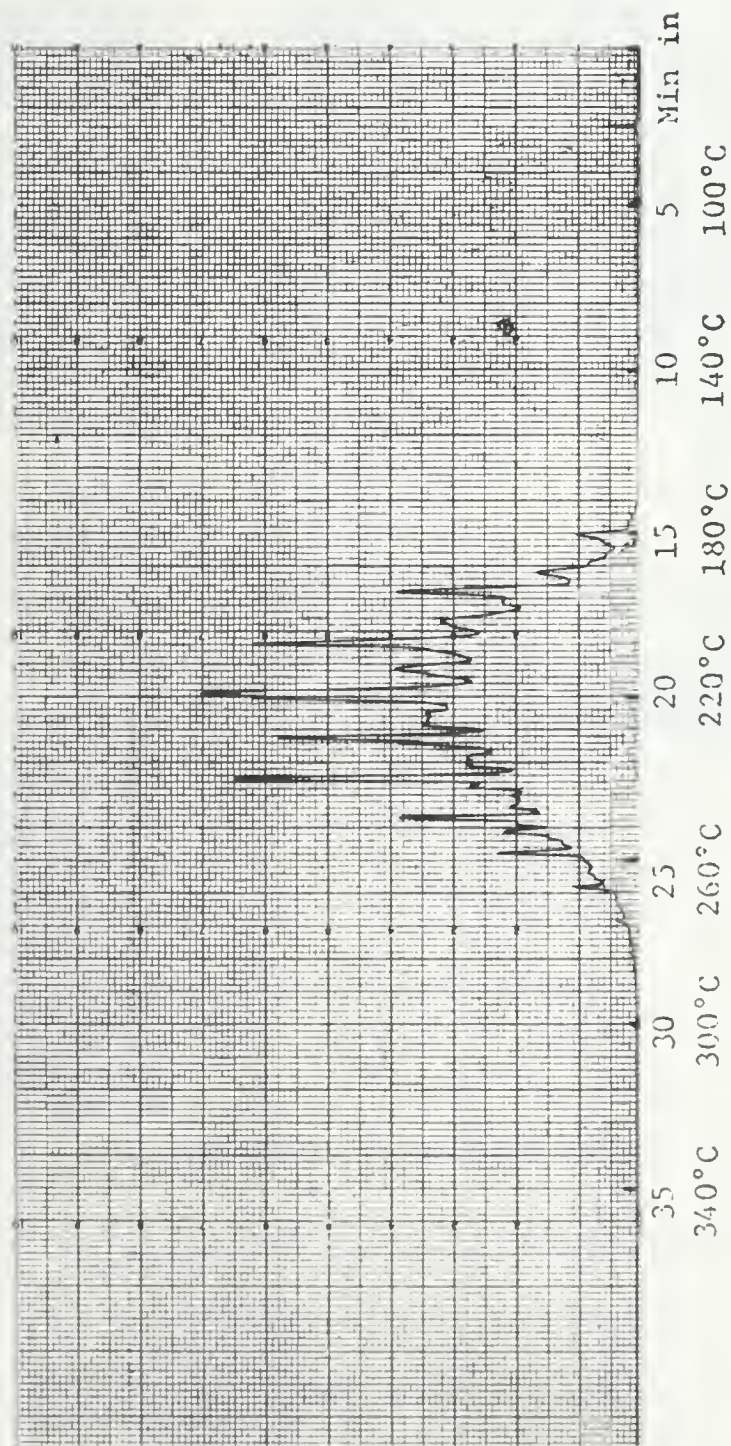


Figure 85. GC Fingerprints of No- 2 Heating Oil 40-A-1 Unweathered and From Accelerated Weathering Experiment (See Section III.2.2)

Column: 15', 1/8", 2% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

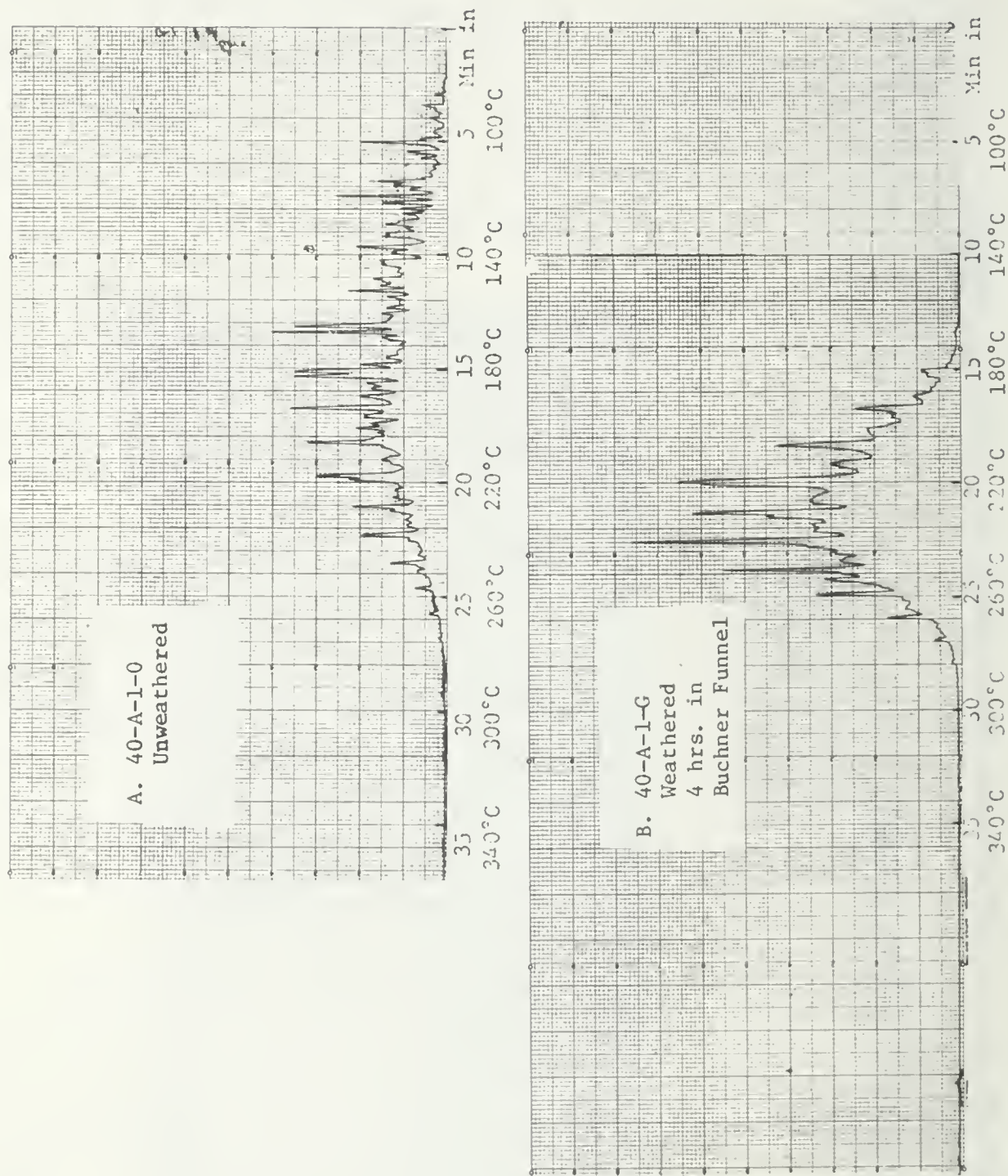


Figure 86. Reversed Phase Liquid Chromatogram of Standard PNA's

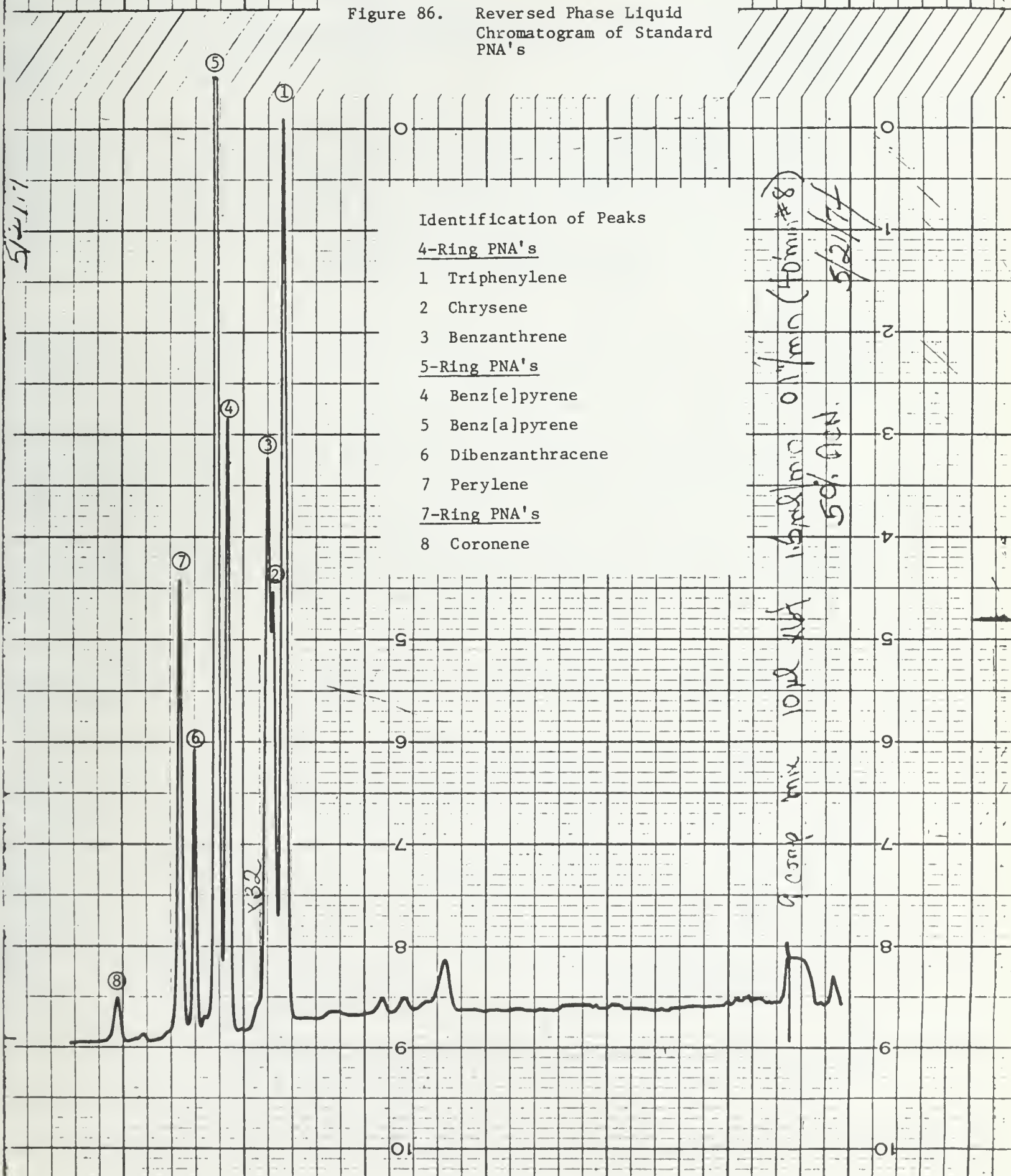
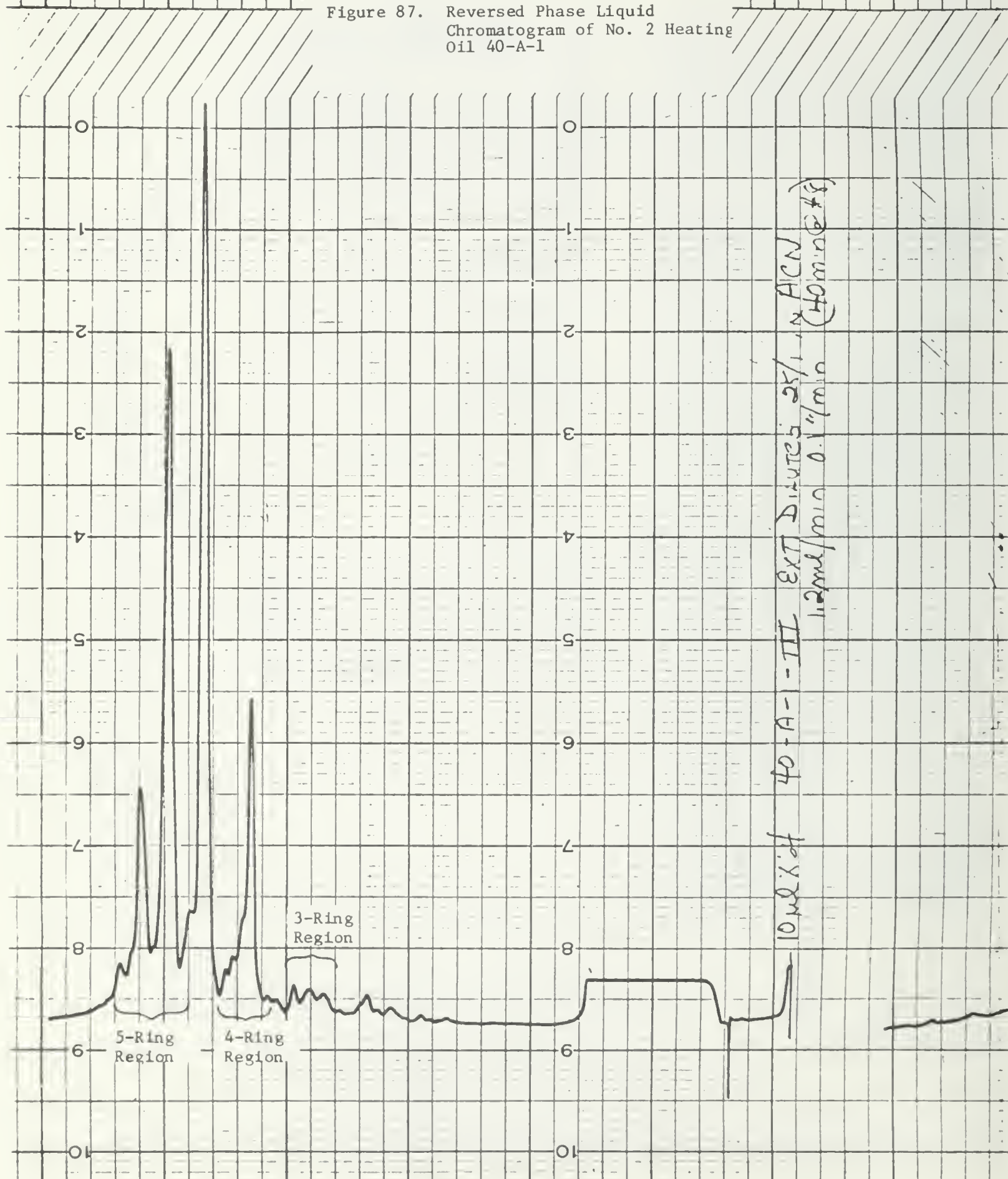


Figure 87. Reversed Phase Liquid
Chromatogram of No. 2 Heating
Oil 40-A-1



IV.9 Reproducibility of the Analytical Data

The precision and reproducibility of GC distillation and specific gravity data was pointed out in Sections III, IV.2 and IV.3. Since these methods were not used for all samples, they are not discussed further here.

Of the remaining methods, those with low resolving power, i.e., LC and TLC, have the poorest reproducibility from trial to trial. TLC R_F factors, for instance, will never be exactly reproducible from run to run. As a result, it is common practice to include a standard compound on each plate and refer to R_S values (17,36) where:

$$R_S = \frac{\text{Migration Distance of Test Oil}}{\text{Migration Distance of Standard}}$$

This is due to difficulties in obtaining plates commercial or home-made of exactly the same coating thickness and degree of activation. Our experience has been that R_F factors for No. 2 fuel oil varied from 5-30% for different plates run on different days. It must be emphasized that no attempt was made to enhance reproducibility, by activating plates for example, since lack of reproducibility of R_F factors is no limitation on the method as a classification tool, which is its primary function. This is because the patterns of spots of zones, i.e., relative R_F factors do not vary from plate to plate and the characteristic responses of various petroleum products are easily recognized. On the other hand, if TLC is to be used for purposes of identifying two similar oils, it is essential that the pollution sample and the possible sources be chromatographed on the same plate (see Section V below).

The same comments apply to LC. As recommended in the previous section, pollution samples and possible sources should be chromatographed close together for optimum results.

With both IR and GC techniques reproducibility was quite good for all repeat samples studied. A few examples will suffice. Comparison of the two weathered samples of Navy distillate fuel, 45-X-1-III (Figure 88) serves to establish both the reproducibility of the analytical technique and the weathering experiments since these samples were obtained from two separate two-week trials. The agreement is quite good although there are minor differences in the spectra. A second example is afforded by the spectra of crude oil 10-A-2 (Figures 89 and 90). In this case the samples were weathered nearly a year apart. The one shown in Figure 89 was weathered for about one week under a previous project (1) and the samples stored until the spectra were run several months later. Figure 89 shows comparable samples of the same oil weathered under the present contract.

Similar comparisons of GC fingerprinting data are shown in Figures 91 and 92. Again agreement is sufficient to permit unequivocal identification.

Figure 88. IR Spectra of Navy Distillate Fuel, 45-X-1, Weathered for Two Weeks in Separate Experiments.

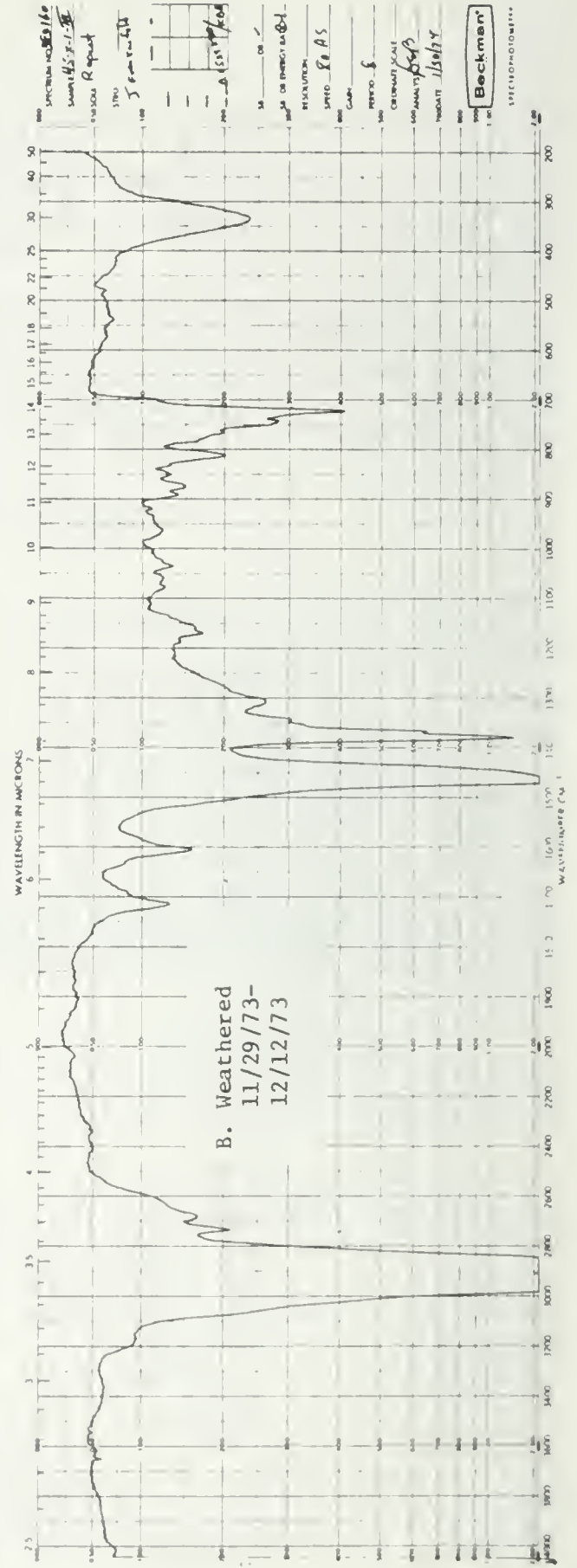
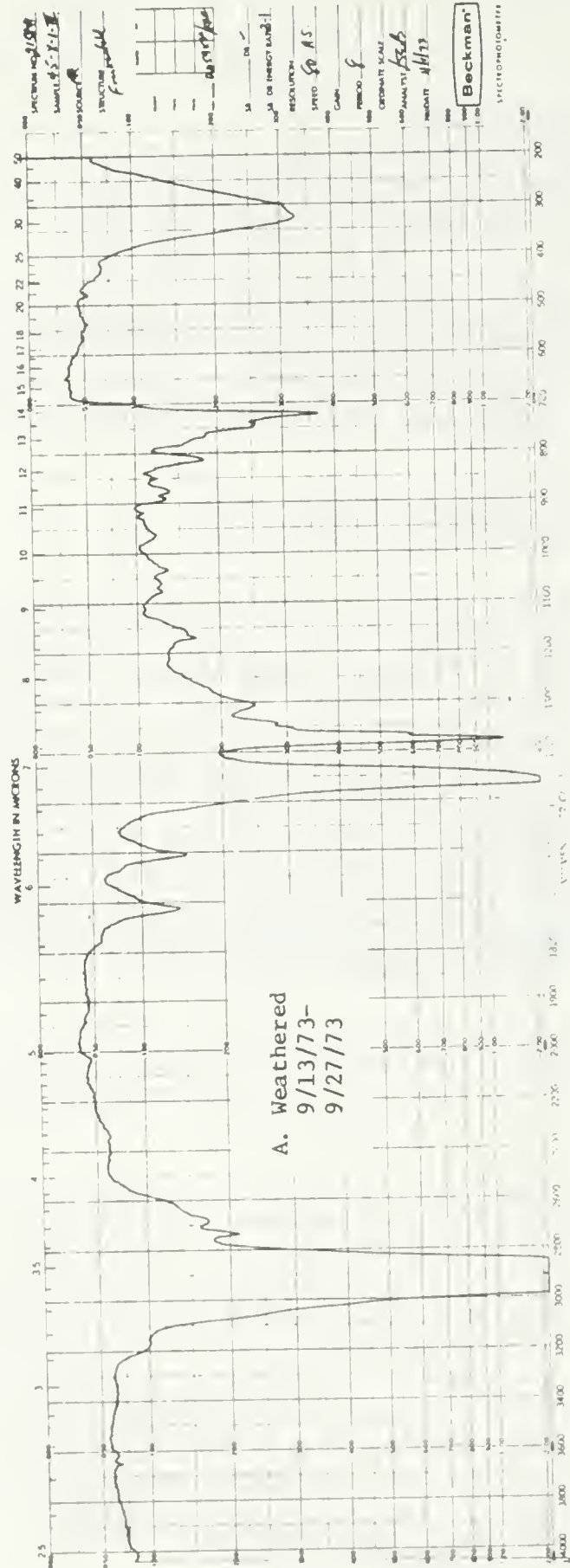


Figure 89. IR Spectra of Crude Oil 10-A-2 From Weathering Experiments in 1972 (Spectra Run in August 1973).

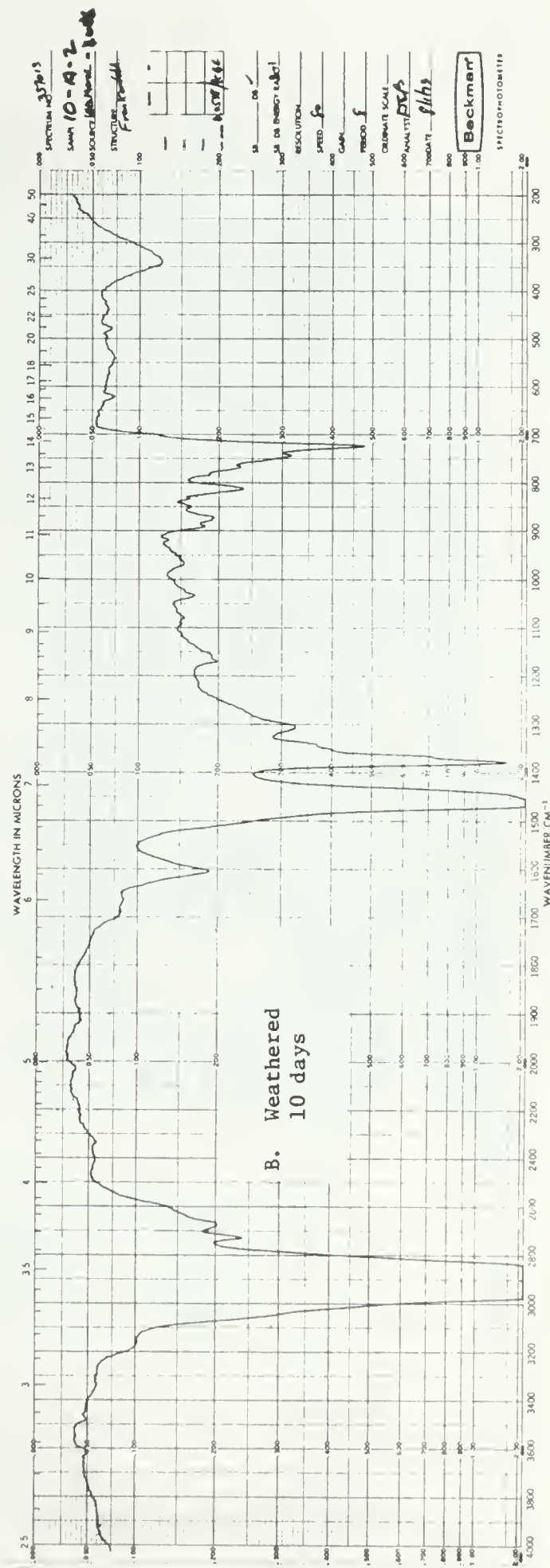
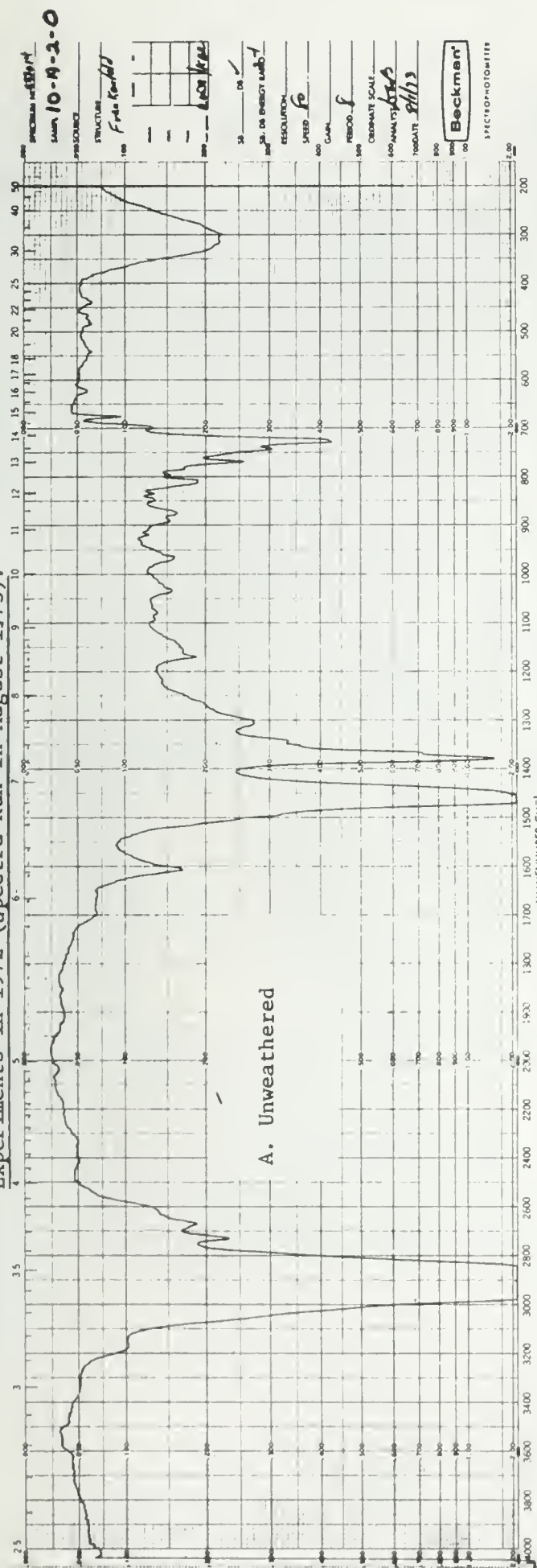


Figure 90. IR Spectra for Crude Oil 10-A-2 From Weathering Experiments in 1973

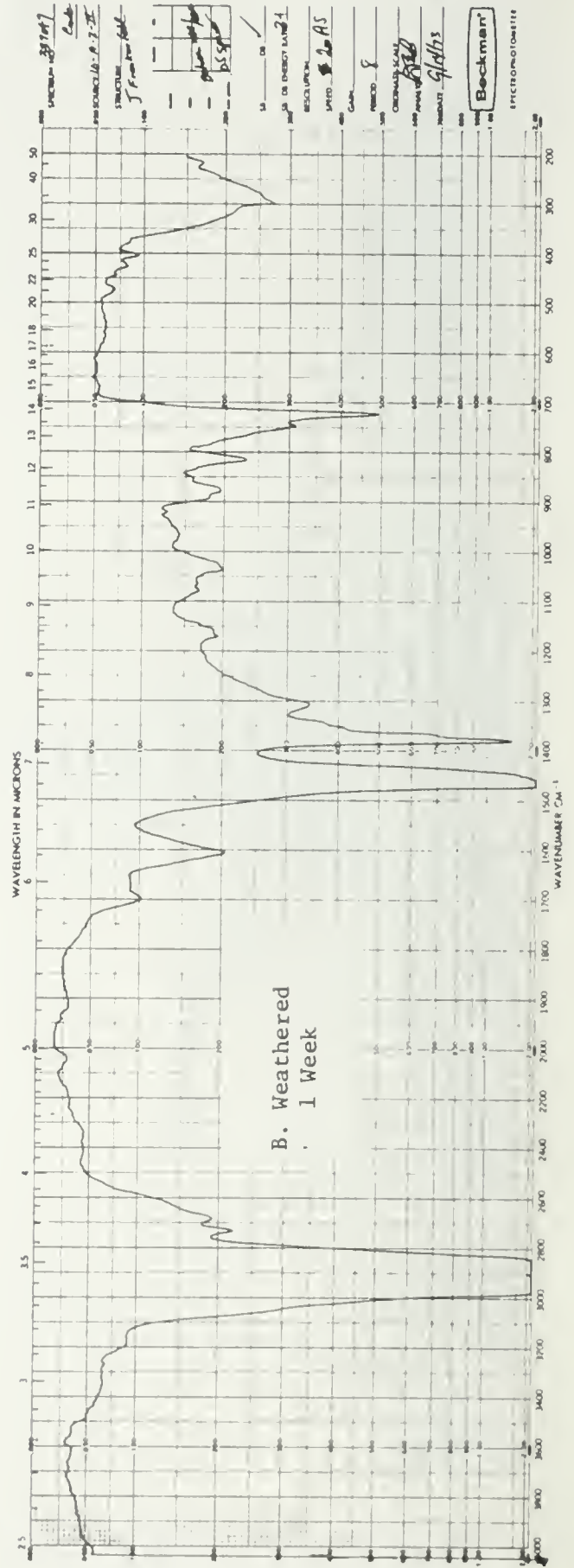
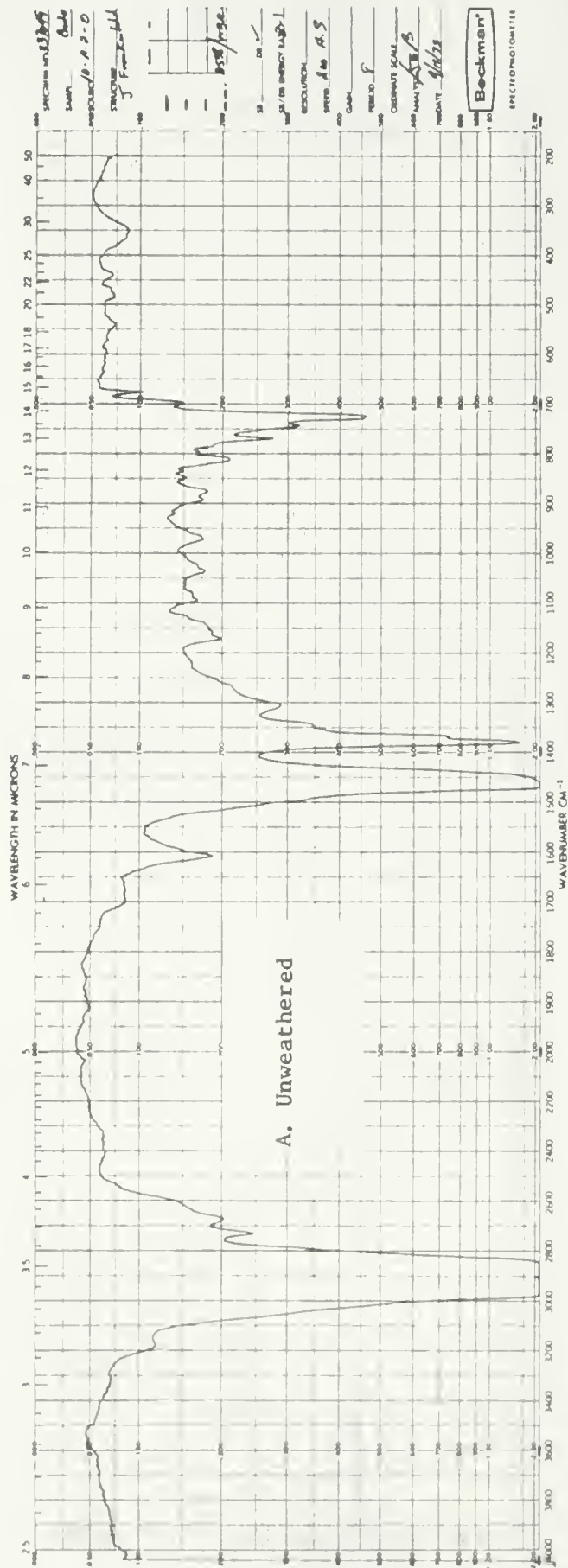


Figure 91. GC Fingerprint of Two Samples of Navy Distillate Fuel,
45-X-1 Weathered in Separate Experiments (two week weathering)

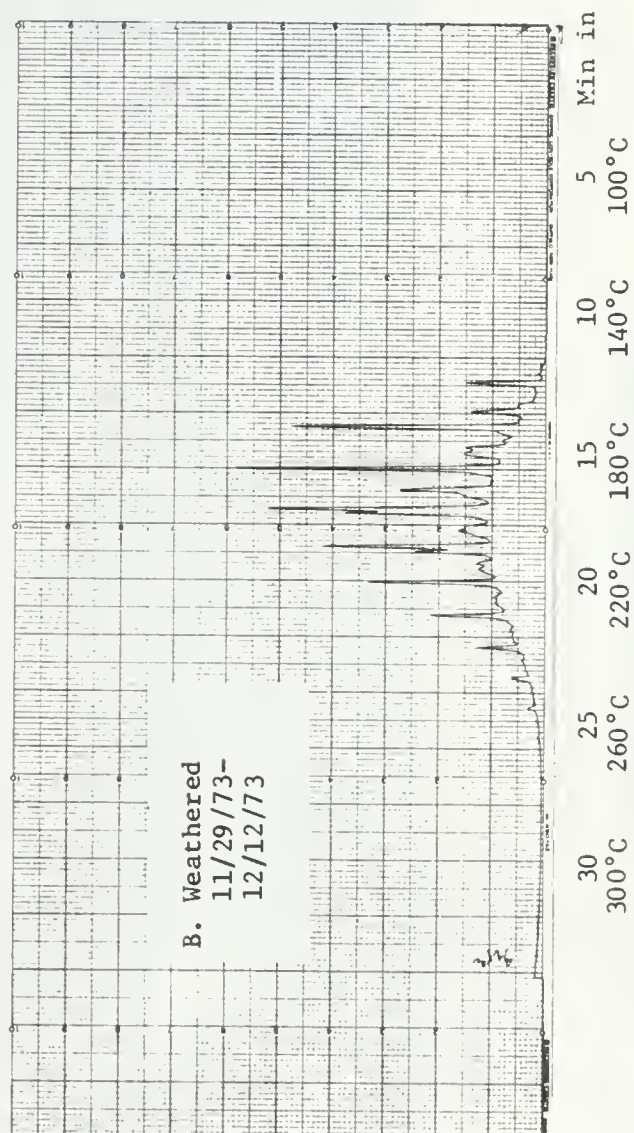
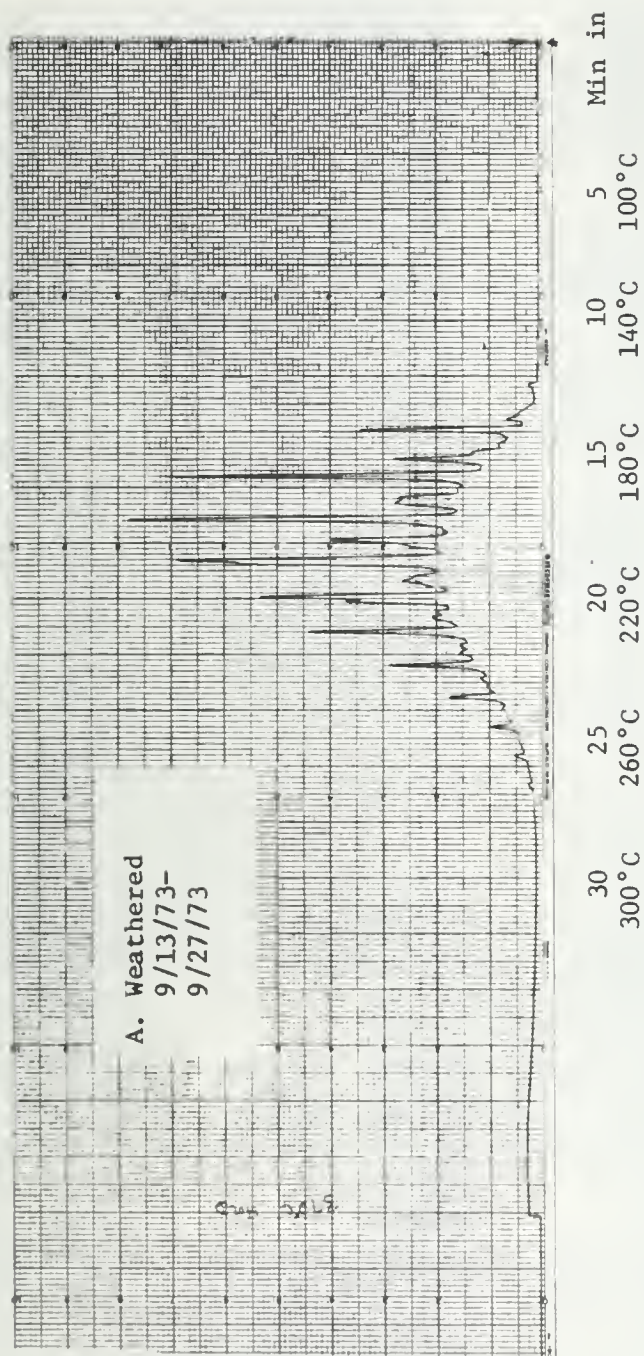
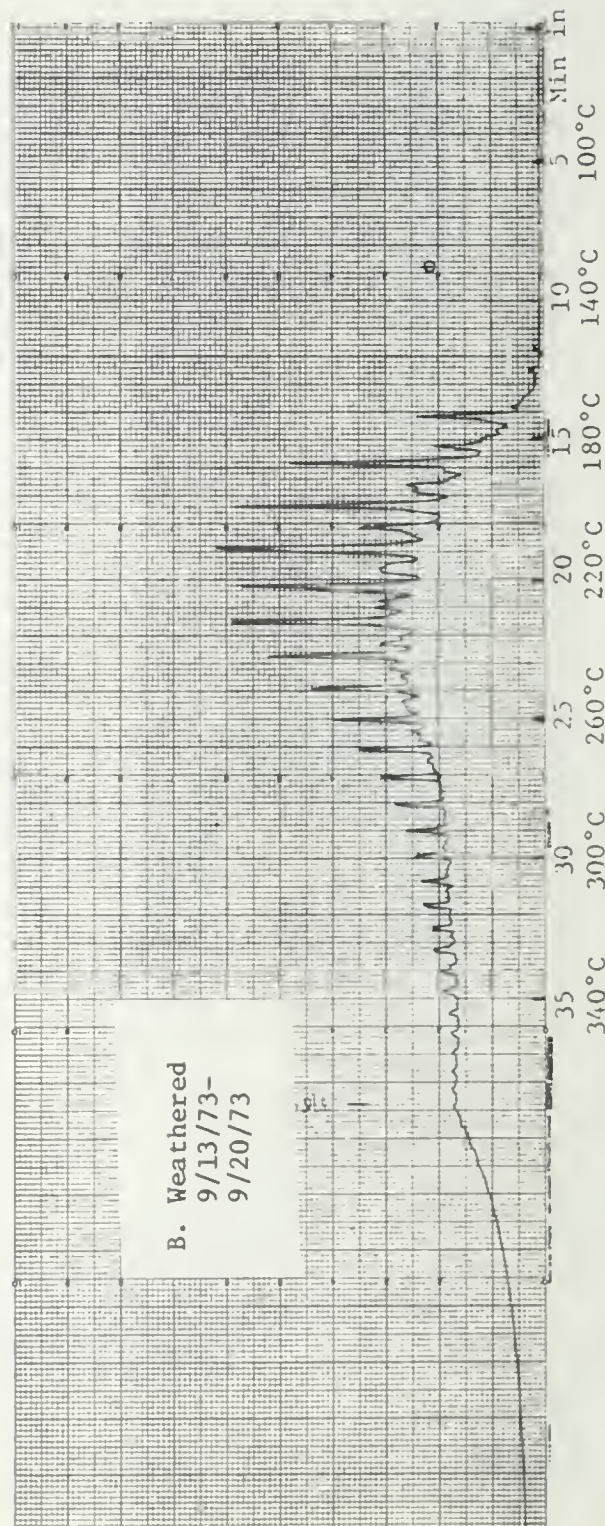
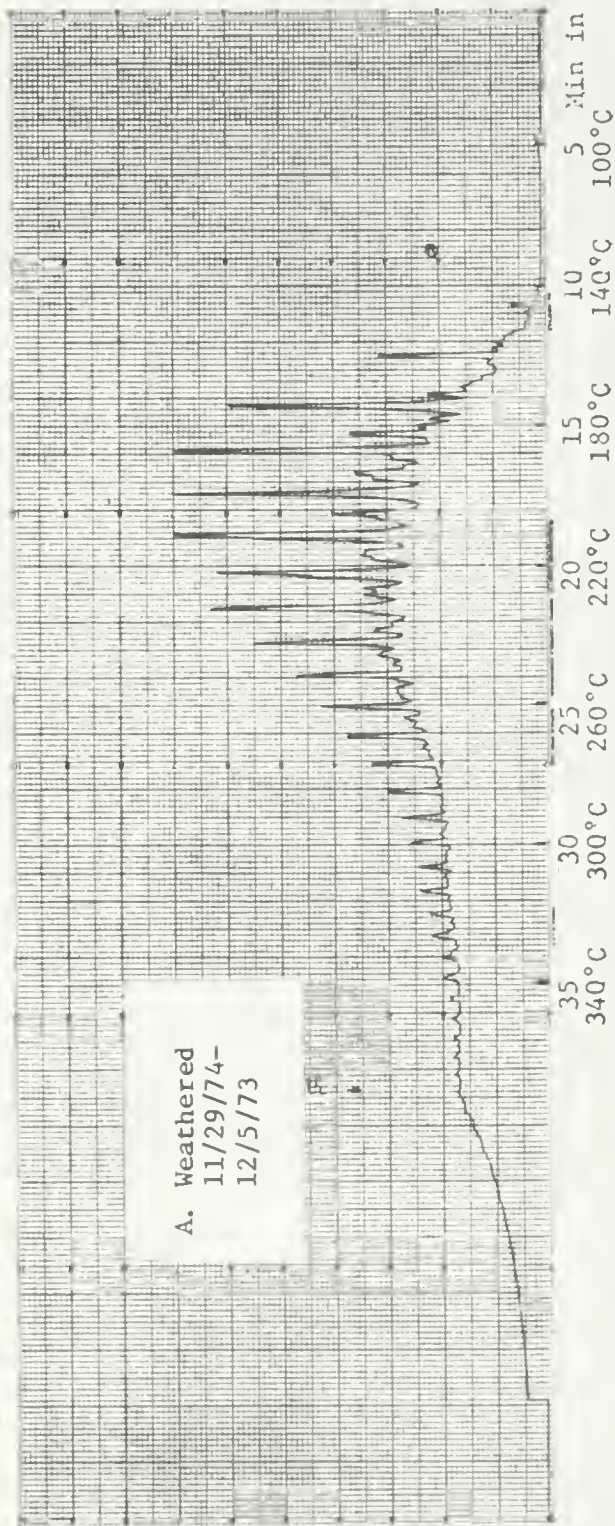


Figure 92. GC Fingerprint of Two Samples of Navy Special Fuel, 33-X-1
Weathered in Separate Experiments (One-Week Weathering)

Column: 15', 1/8", 3Z SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min



V. SYSTEM SELECTION AND EVALUATION

This section represents completion of Task (5) System Selection and Refinement. In addition several examples will be presented to show how the integrated system would be used to classify and identify some hypothetical "unknowns".

From the previous discussions, it is clear that we recommend the following four techniques for finger printing on oil spills. They are broken down as largely classification or identification techniques although it must be emphasized that considerable cross-over would occur.

RECOMMENDED TECHNIQUES

Classification Methods

Thin-Layer Chromatography
Liquid-Liquid Chromatography

Identification Methods

Infrared Spectroscopy
Gas Chromatography

It is strongly recommended that capabilities be maintained in at least three and preferably all four of these methods. No one method, nor likely even two, will be sufficient to uniquely identify pollution samples of all types of petroleum products. Each method has its special value and area of application but none is completely effective by itself. This does not mean that all methods need be used each time. Usually preliminary classification will suggest the best follow-up for final identification. How the system might work is illustrated by the following hypothetical examples.

V.1 Example 1. Classification and Identification of a Lube Oil Pollutant

The pollution sample coded "X" is first centrifuged to remove suspended water, and then analyzed using the methods described above. The GC fingerprint (Figure 93) indicates the material is a heavy, highly refined product but cannot say unequivocally of what type. The TLC analysis is shown in Figure 94A and B. The material is clearly a lube oil but, from examination of the additive pattern in Figure 94B, not the "standard" lube, in this case 50-A-1.

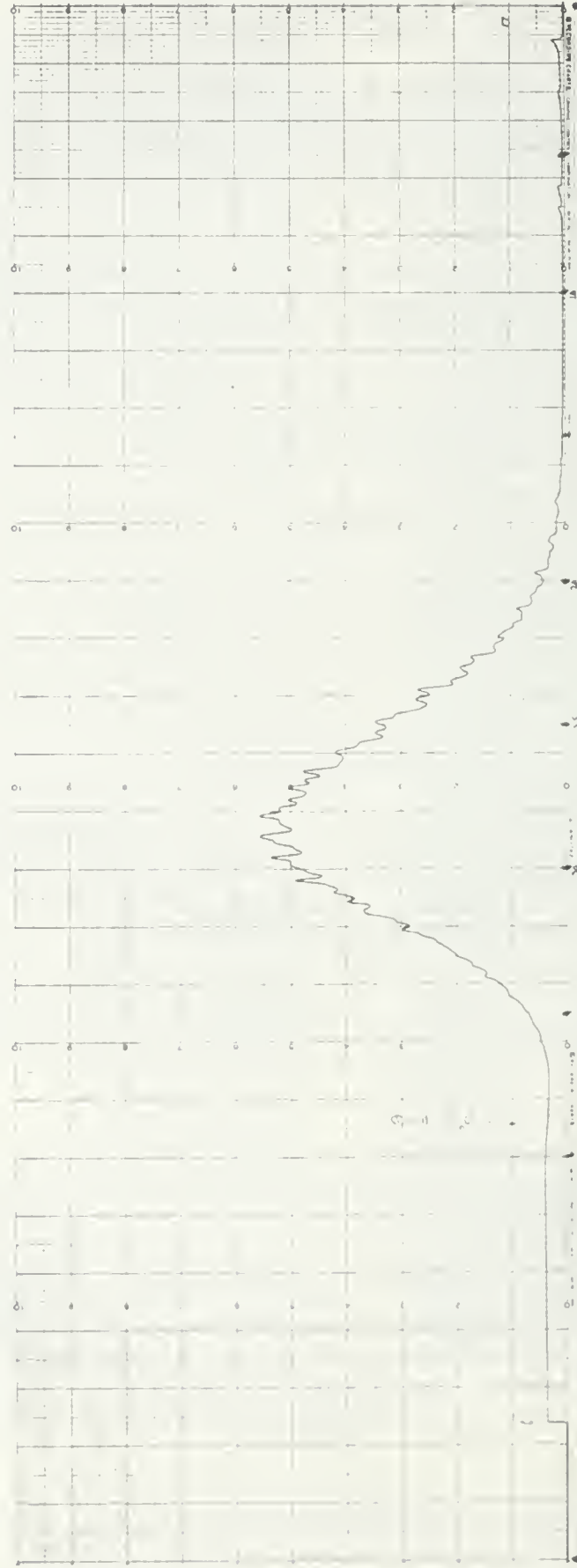
Authentic samples of three possible sources of the pollution (Lube Oils 50-A-1, 50-C-2 and 50-G-2) are now obtained and chromatographed along with "X" (Figure 95A and B). This sample is readily identified as 50-C-2. Confirmation is readily obtained from the infrared spectra

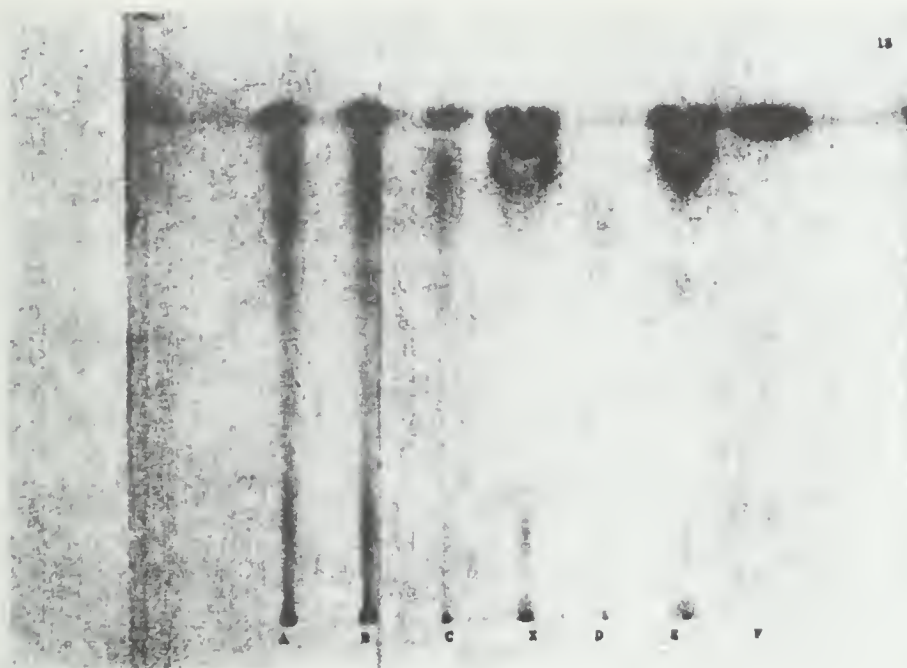
Figure 93. GC Fingerprint of Suspected Lube Oil Pollutant "X"

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min





A. Detection by $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$



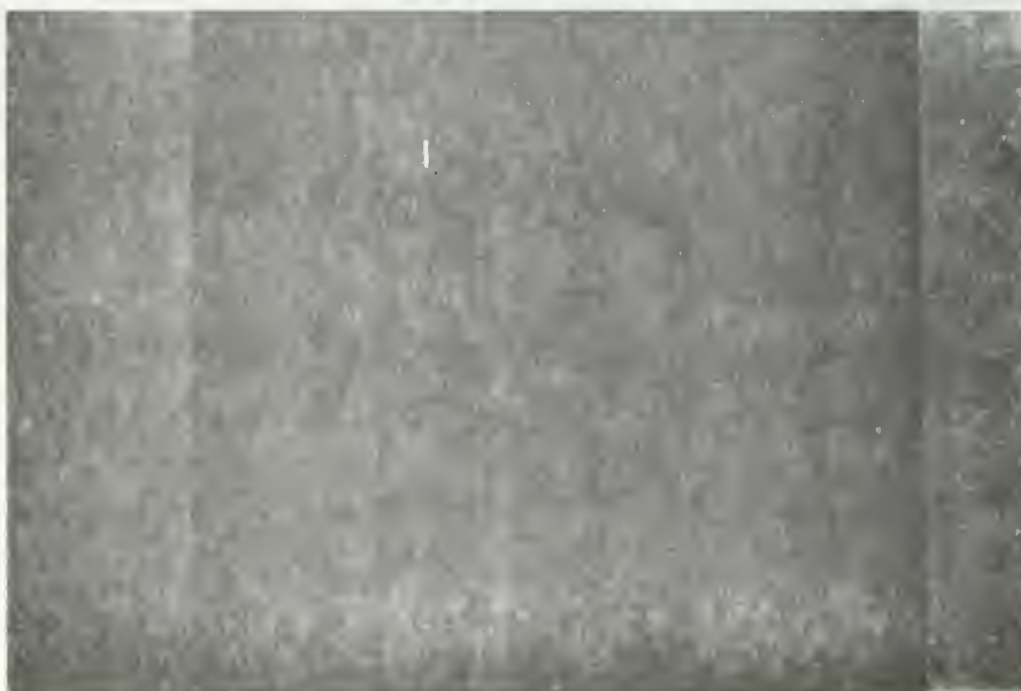
B. Detection with I_2 Vapor

Figure 94. TLC Classification of Unknown Lube Oil "X".
A. Crude Oil 10-A-1-III; B. Residual Oil 20-A-1-III;
C. Blended Residual Oil 30-A-1-III; D. Distillate Fuel
Oil, 40-A-1-III; E. Lube Oil 50-A-1-III; F. White Oil
60-X-2-III.



A

A. 50-G-2; B. 50-C-2; C. 50-A-1



B

A. 50-G-2; B. 50-A-1; C. 50-C-2

Figure 95. TLC of Pollutant "X" and Three Suspect Sources

Figure 96. IR Spectra of Suspected Lube Oil Pollutant and Three Possible Sources

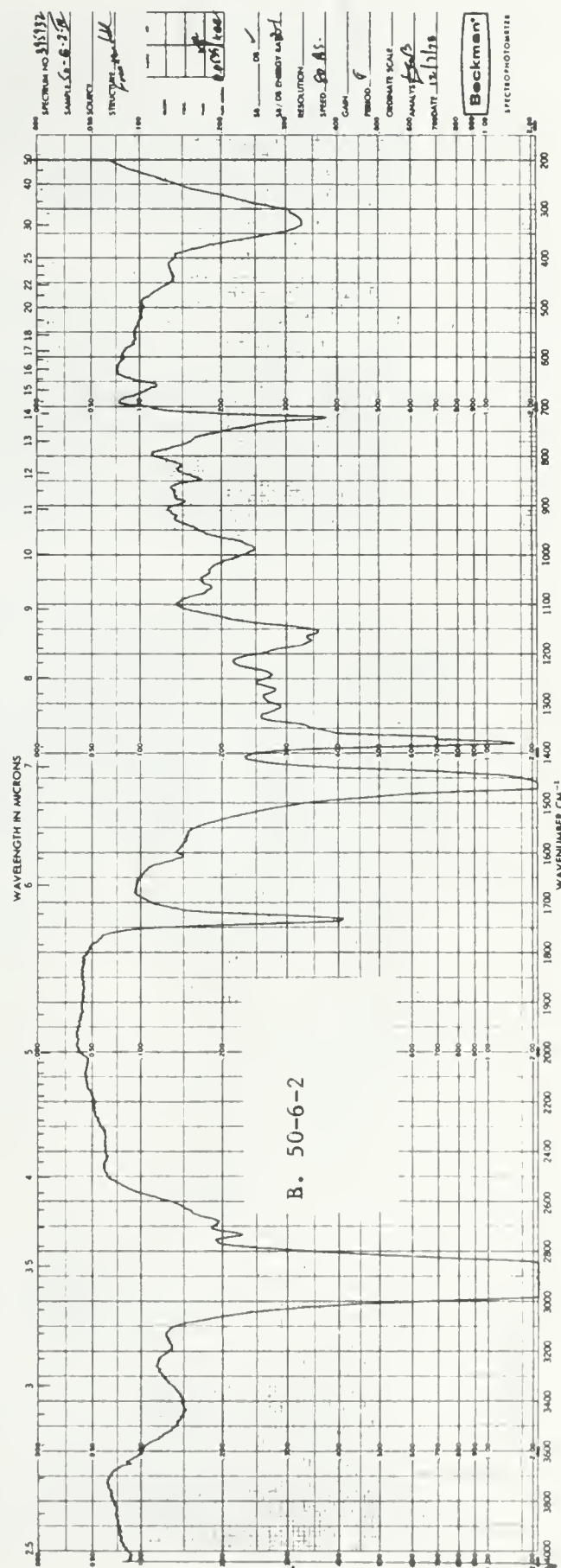
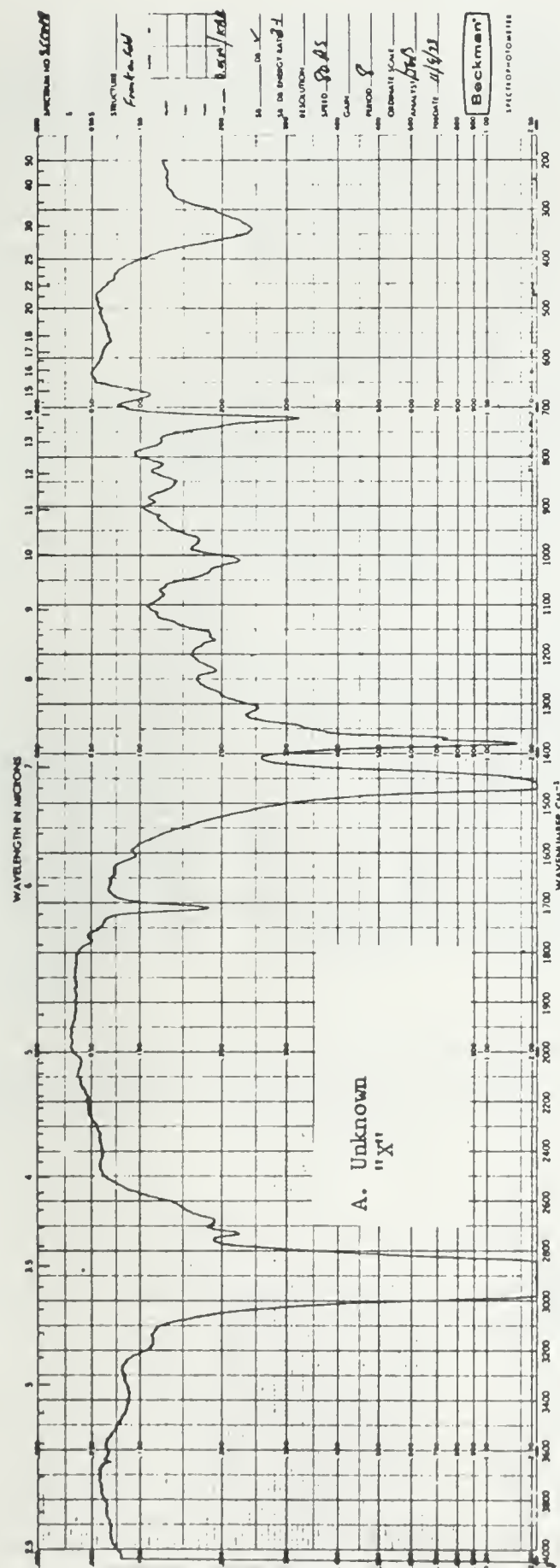
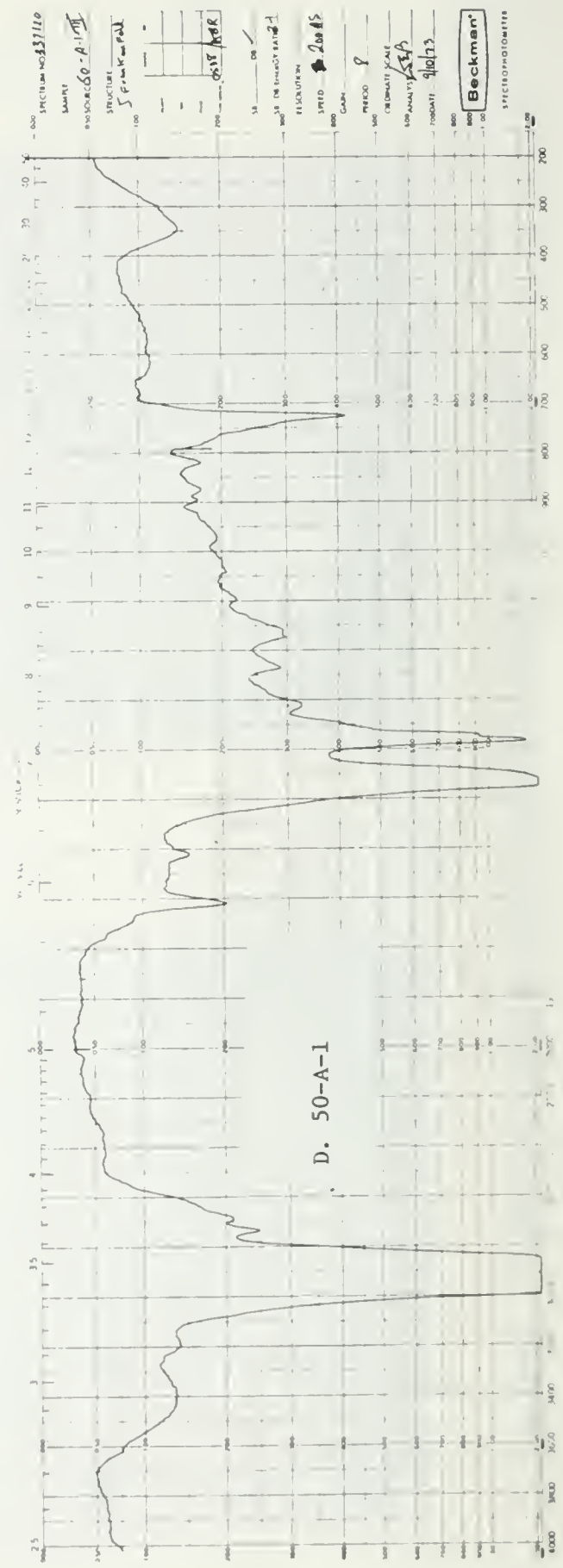
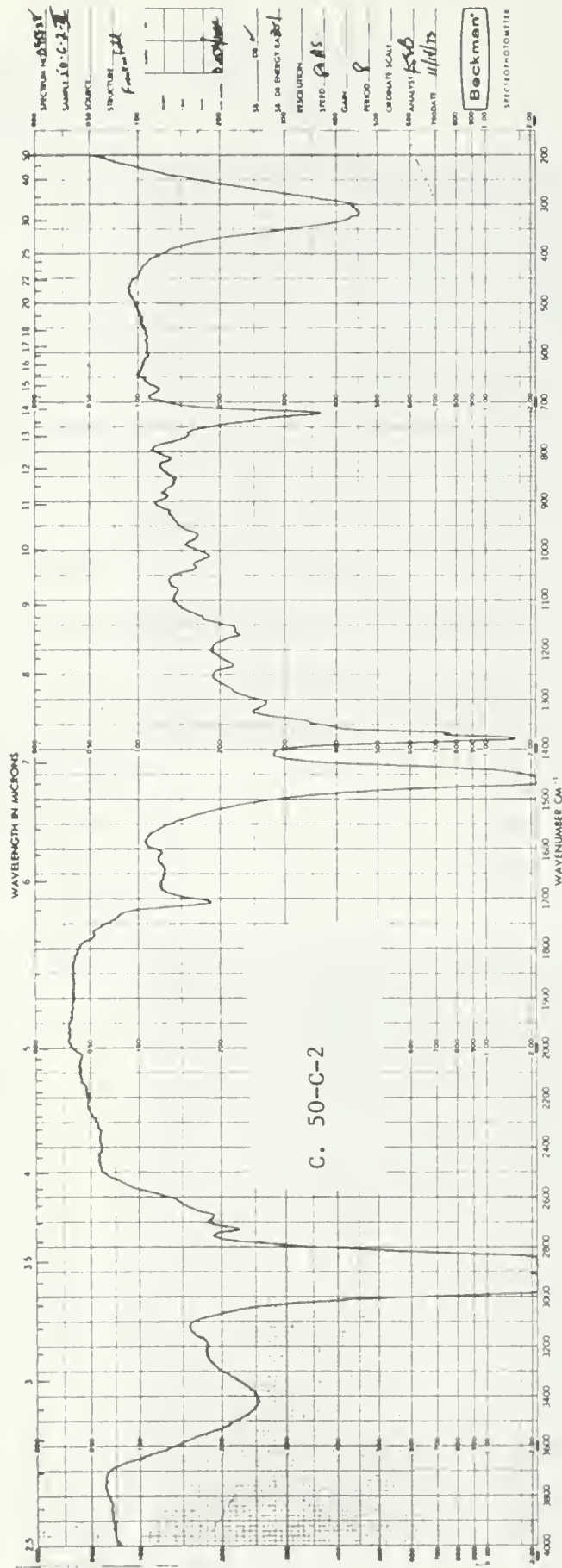


Figure 96. (Cont'd)



(Figure 96A-D). The pollution sample, while not identical, due to weathering differences, is still much more similar to 50-C-2 (compare Figures 96A and C). Note the combination of absorbance peaks at 975 cm^{-1} , 1010 cm^{-1} , 1155 cm^{-1} and 1710 cm^{-1} and lack of absorption at 1175 cm^{-1} and lack of absorption at 1175 cm^{-1} , 1275 cm^{-1} and 1740 cm^{-1} which, taken together rule out the other two possibilities.

V.2 Example 2. Classification and Identification of Crude Oil Pollutant

The spill sample, "X" is treated and analyzed as described in the previous example. The TLC chromatogram (Figure 97) indicates "X" is a crude oil or a residual fuel. The smooth distribution of hydrocarbons observed in the GC fingerprint (Figure 98A) strongly suggests "X" is a crude although a straight run resid (bunker) or even a blended resid with the light ends gone cannot be ruled out.

Also shown in Figure 98 are four possible sources for the spill, three fresh crudes and a residual oil. The spill sample is clearly most similar to crude oil 10-A-10 (Figure 98D). Note the unusual rippling effect in the paraffin peaks at long retention times, the large peak, due to pristane at about 17 min. retention time and the characteristic doublets at 17 and 18 min. These are easily distinguished even when comparing the weathered sample with the fresh crude. It would, however, have been easier to make the identification if artificially weathered crudes were used. The most similar fresh crude other than the actual source is 10-A-3 (Figure 98C). The GC fingerprint for a weathered sample is shown in Figure 99. The differences in peak ratios in this trace and that of Figure 98A are more easily seen.

Confirmation of the identification of "X" as crude oil 10-A-10 is obtained by measuring the critical peak ratios. These are compared in Table 24. The only reasonable fit is with "X" and 10-A-10.

Table 24

GC Peak Ratios for Crude Spill Sample X and Four Suspect Sources

<u>Oil*</u>	<u>Pristane/Phytane</u>	<u>C₁₇/Pristane</u>	<u>C₁₈/Phytane</u>
"X"	2.9	0.62	1.4
10-B-1	0.94	3.9	3.0
10-A-3	1.7	0.79	1.1
10-A-10	2.8	0.65	1.7
20-A-1	1.0	1.9	1.7

- - - - -

* Unweathered except for "X".

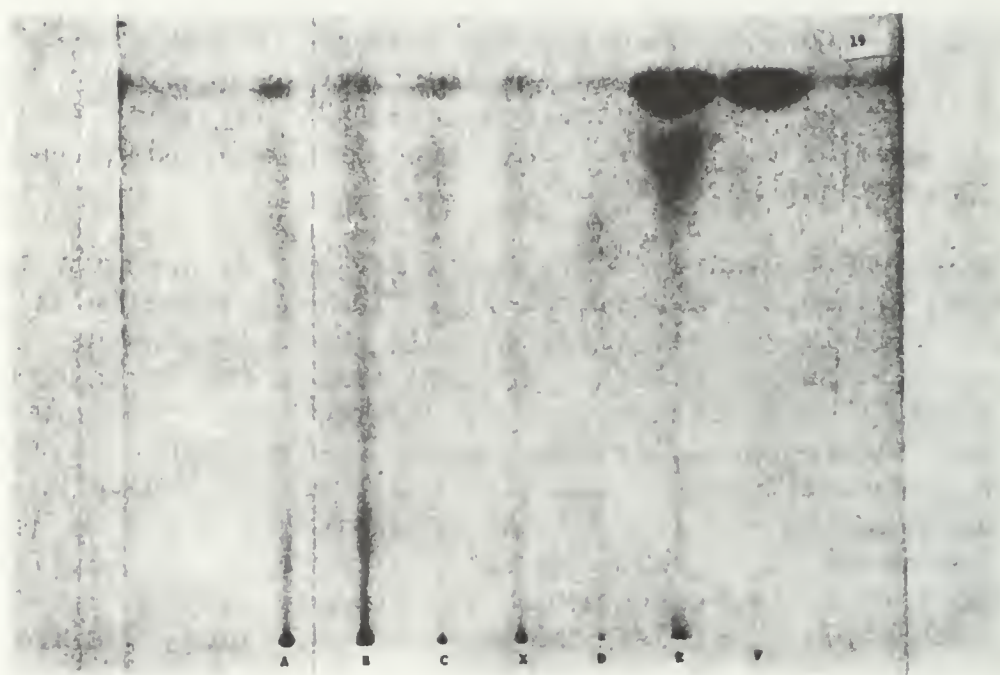


Figure 97. TLC Classification of Suspected Crude Oil Pollution Sample

A. Crude Oil 10-A 1-III; B. Residual Fuel, 20-A-1-III;
C. Blended Residual Fuel 30-A-1-III; D. Distillate Fuel
40-A-1-III; E. Lube Oil 50-A-1-III; F. White Oil 60-X-2-III.

Figure 98. GC Fingerprint of Unknown Spill Sample Crude Oil
Type and Four Suspected Sources

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min

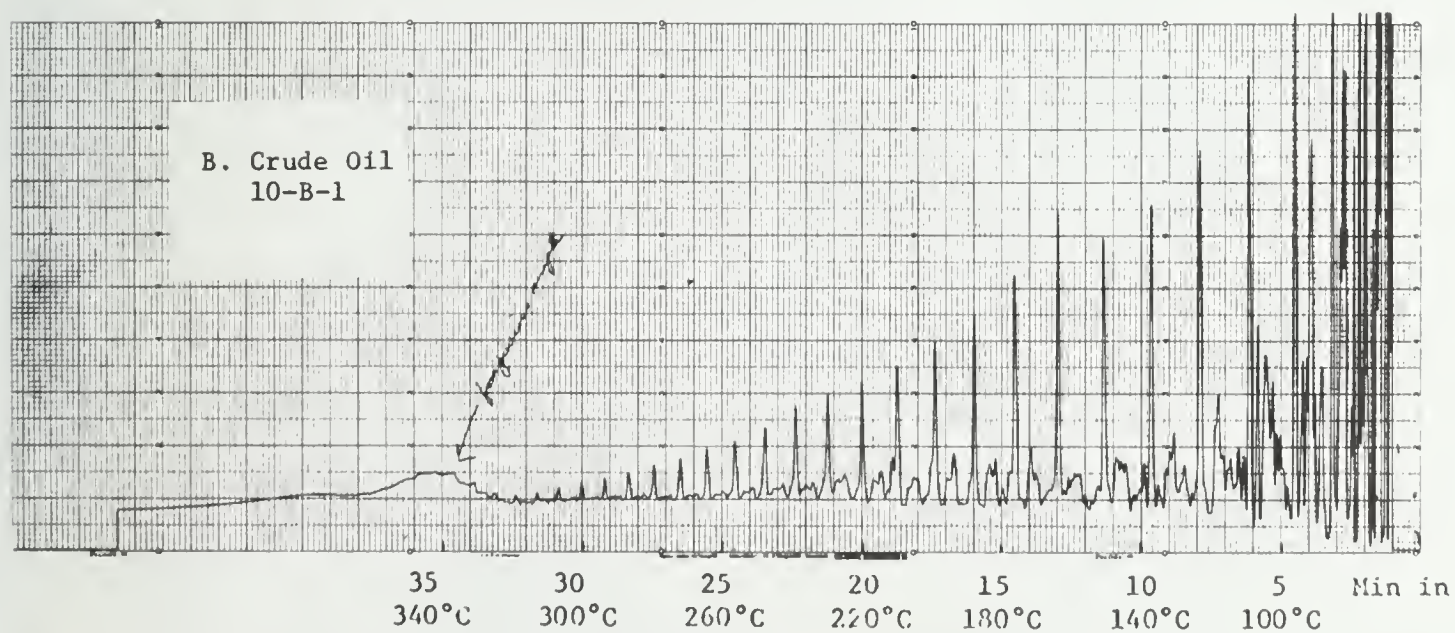
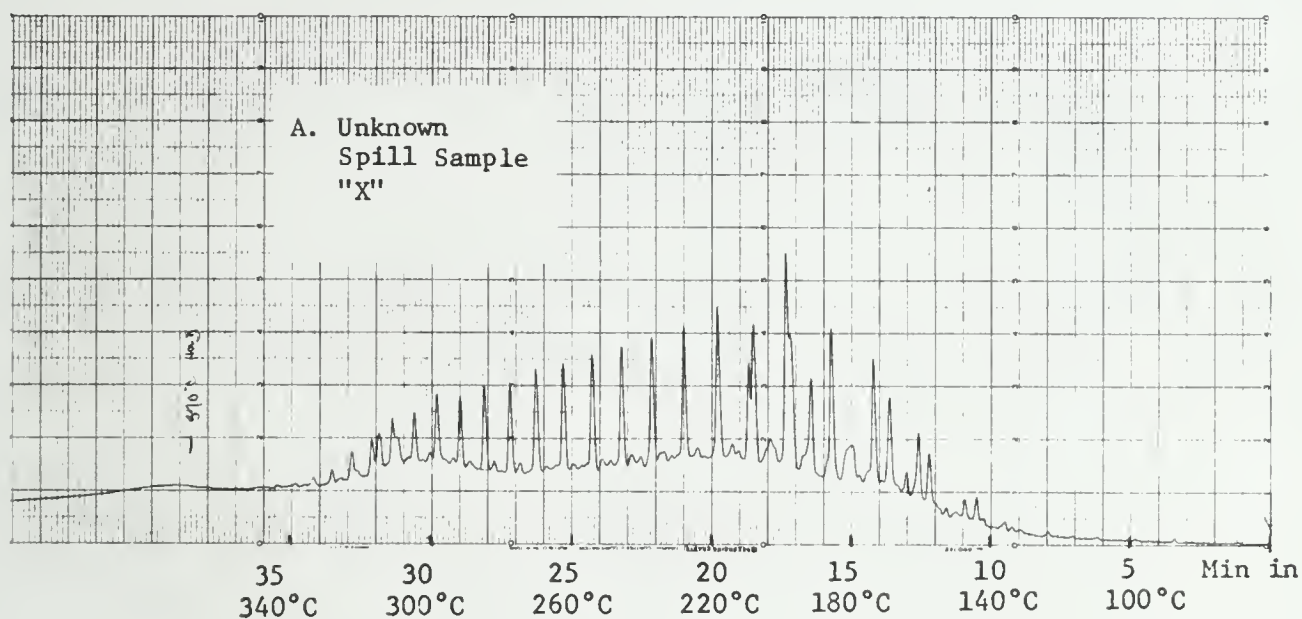


Figure 98. (Contd)

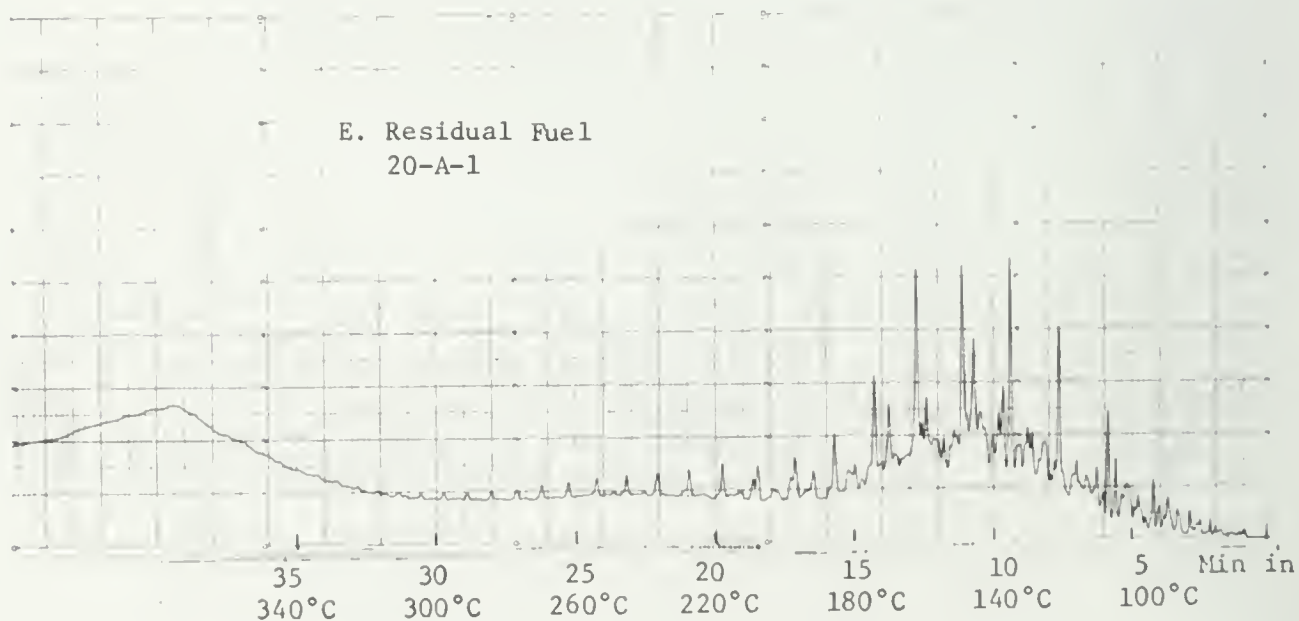
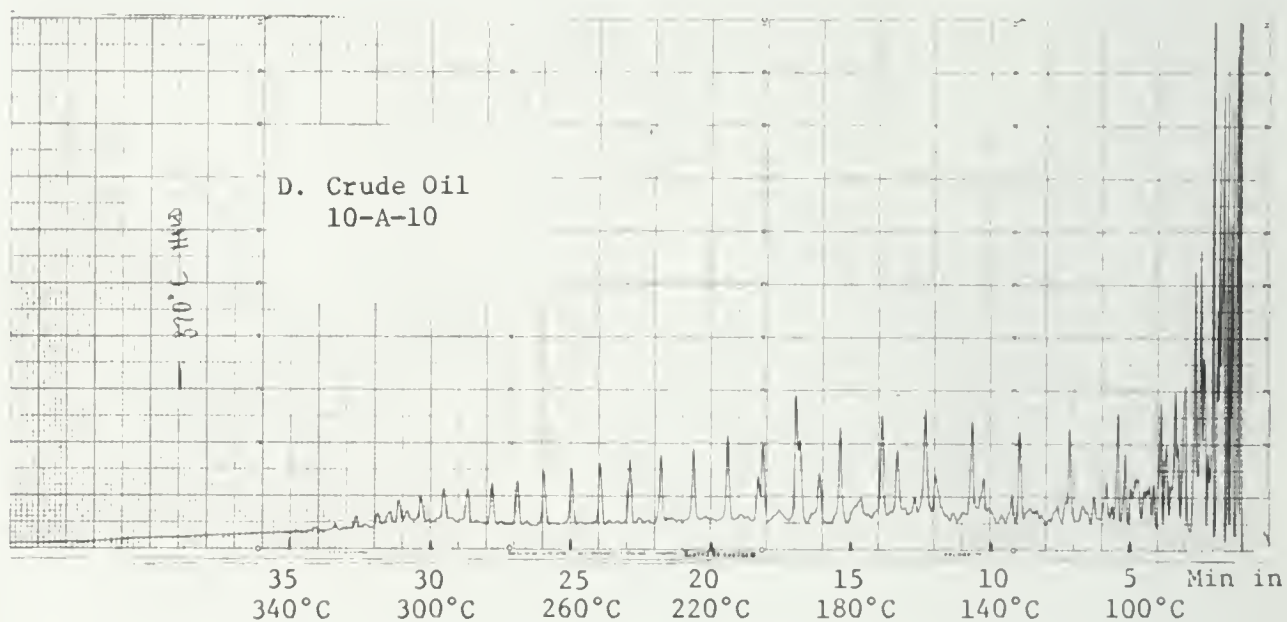
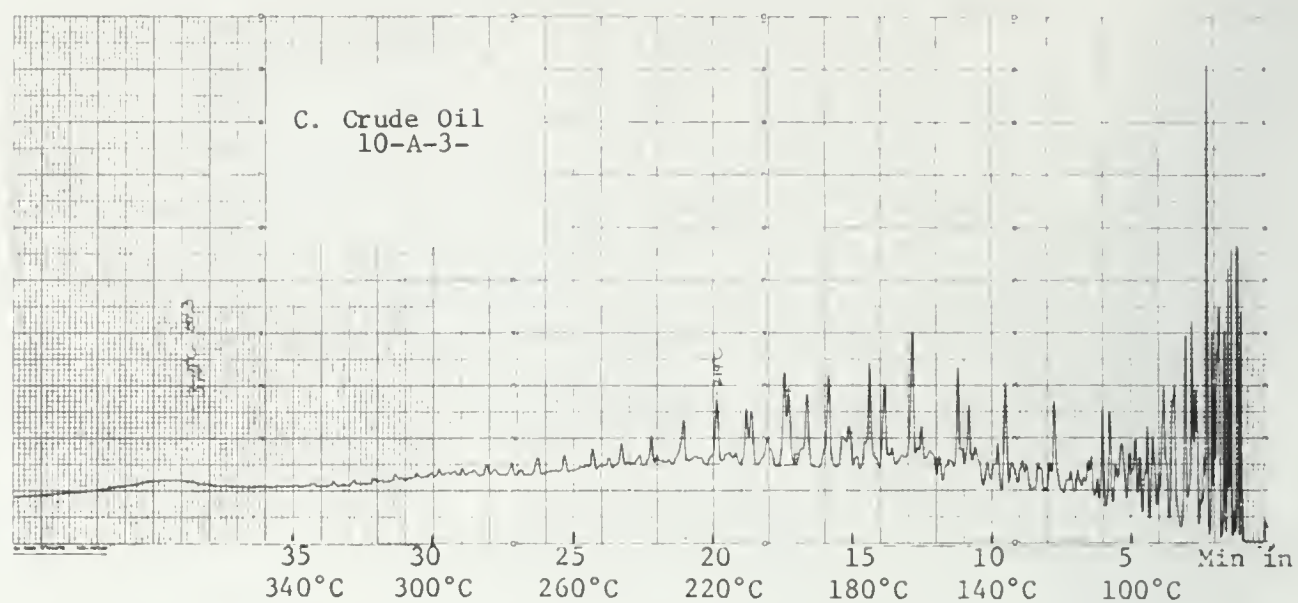
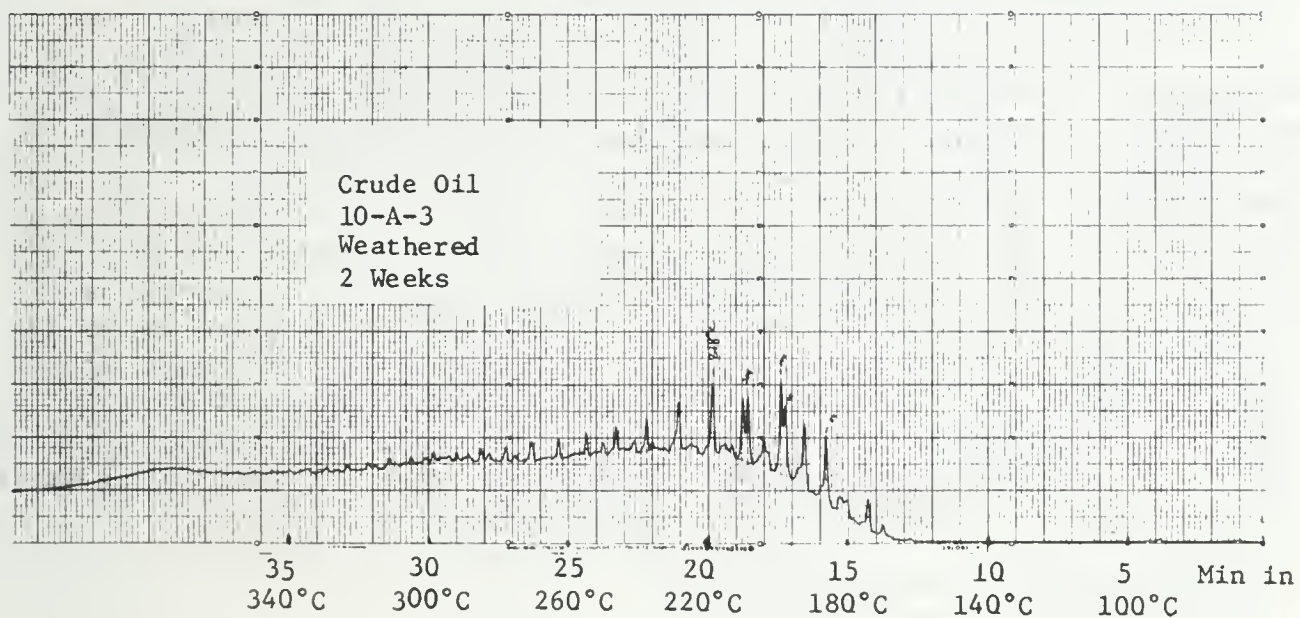


Figure 99. GC Fingerprint of Suspected Crude Oil 10-A-3-
Weathered Sample

Column: 15', 1/8", 3% SE-30 on 80/100 Supelcoport

Program: 60°C - 370°C, 8°/min

Chart Speed: 1/2"/min



It is interesting to note that the infrared fingerprints for this series while useful would not be sufficient for an unequivocal identification. As seen in Figure 100A and B, two suspect sources 10-B-1 and 10-A-10 are very similar and identification of a weathered sample with one of these could not be established with confidence. The other two suspect samples have somewhat different spectra (Figures 100C and D).

The following examples illustrate the use of liquid chromatography in two actual cases where other methods gave equivocal results.

V.3 Differentiating Between Three Similar Heating Oils by Liquid Chromatography

The three No. 2 heating oils, 40-A-1, 40-A-4 and 40-A-5 have quite similar IR fingerprints (Figure 101)* as well as other properties (31). A method for distinguishing them was needed and they were analyzed by liquid-liquid chromatography as described above. The chromatograms are given in Figures 102-104. The oils 40-A-4 and 40-A-5 are easily distinguished by either the RI (Figure 102) or UV detection methods (Figure 103). The UV traces for samples 40-A-1 (Figure 104, bottom) and 40-A-4 (Figure 103A) are very similar. The RI traces (compare Figures 104, top and 102A) are quite different, showing a reversal in relative sizes of the naphthalene and xylene peaks. On the other hand, the RI chromatograms of 40-A-1 (Figure 104, top) and 40-A-5 (Figure 102B) closely resemble each other but the UV traces (Figures 104, bottom and 103B) do not. By using both detectors these three heating oils are easily distinguished.

V.4 Differentiating Two Residual Fuel Oils by Liquid Chromatography

Two samples of residual fuels, obtained by the U.S. coast Guard R&D Laboratories as possible pollution samples (37) were considered to be of the No. 4 (30-I-1) and No. 6 (32-I-1) classifications. However, they had very similar physical properties and GC traces (37). The IR spectra (Figure 105) and sulfur contents (both equal to 0.5% S within experimental ranges) while not identical are so nearly so that an additional piece of corroborative evidence was welcome as an aid in differentiating the samples. The liquid-liquid chromatograms for the two samples are shown in Figures 106 and 107. Both the UV and RI traces show significant differences but the former is more useful. The "No. 4" oil (Figure 106) has a greater quantity of the lighter aromatics (peaks A and B). The LC method was useful as confirmation of assignments made by other methods.

- - - - -

* Note that Figure 101A is identical to Figure 24A in Section IV.5. It is reproduced here for ease of comparison.

Figure 100. IR Spectra of Four Suspected Pollution Sources

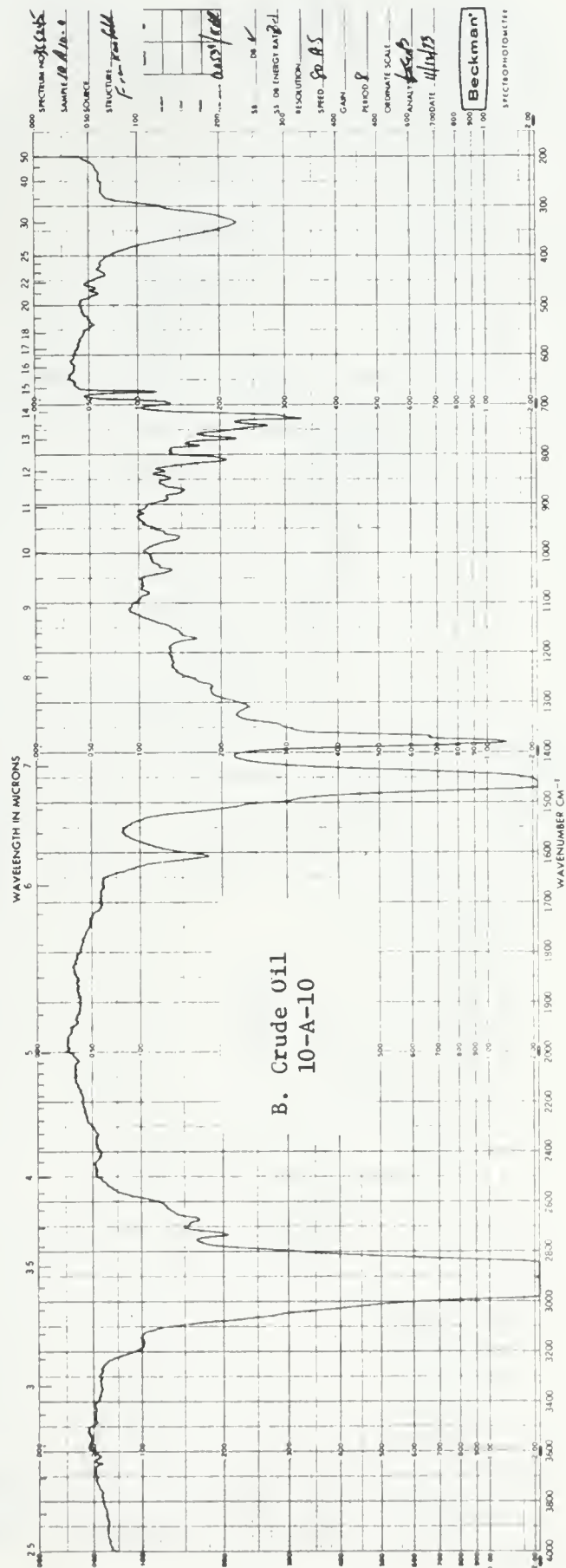
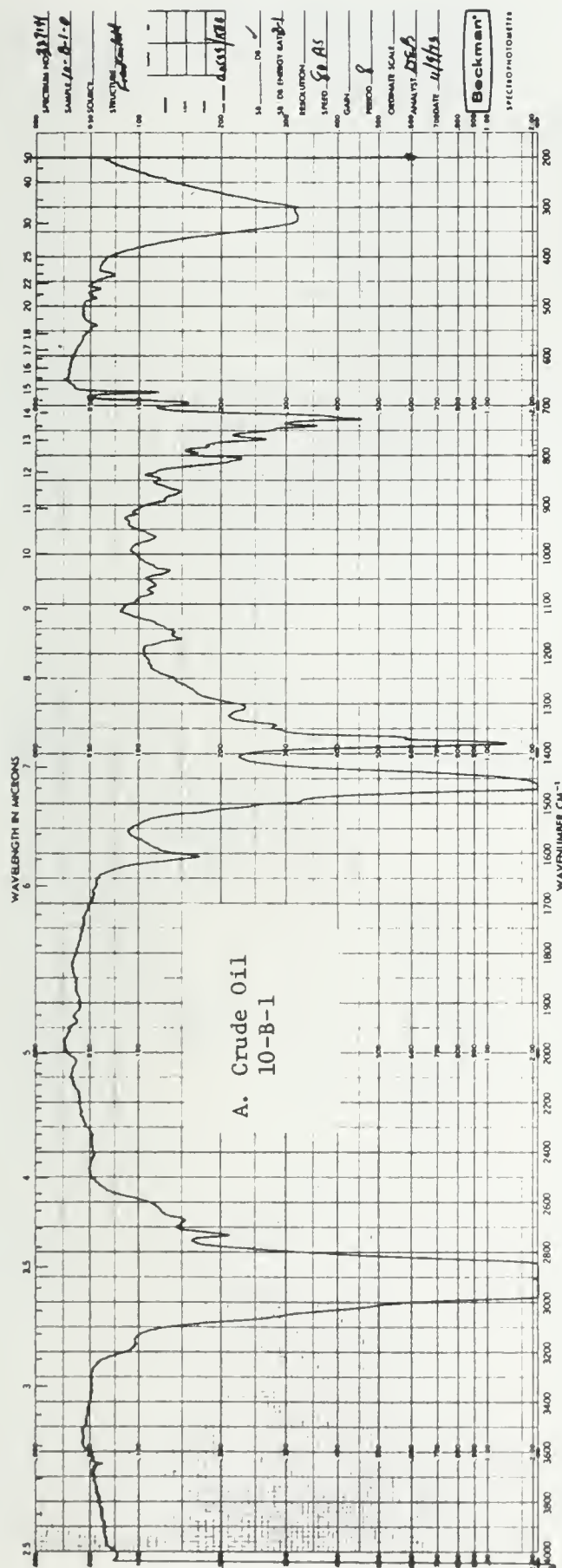


Figure 100. (Cont'd)

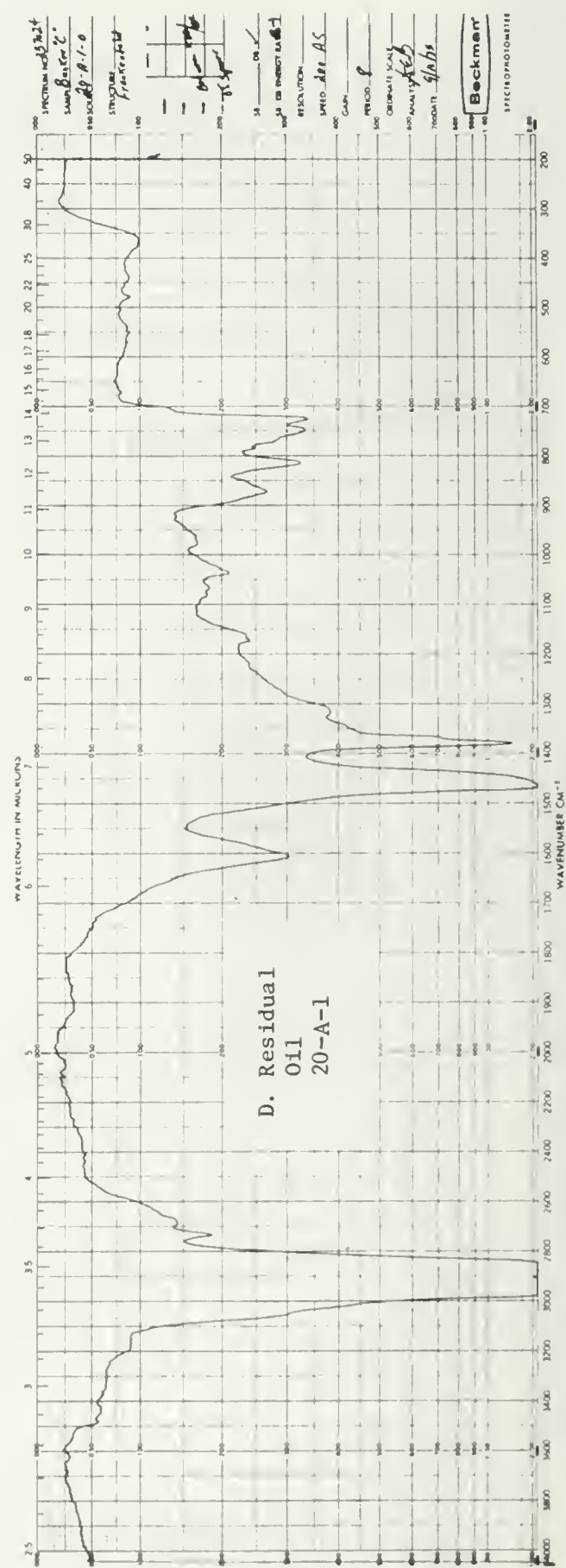
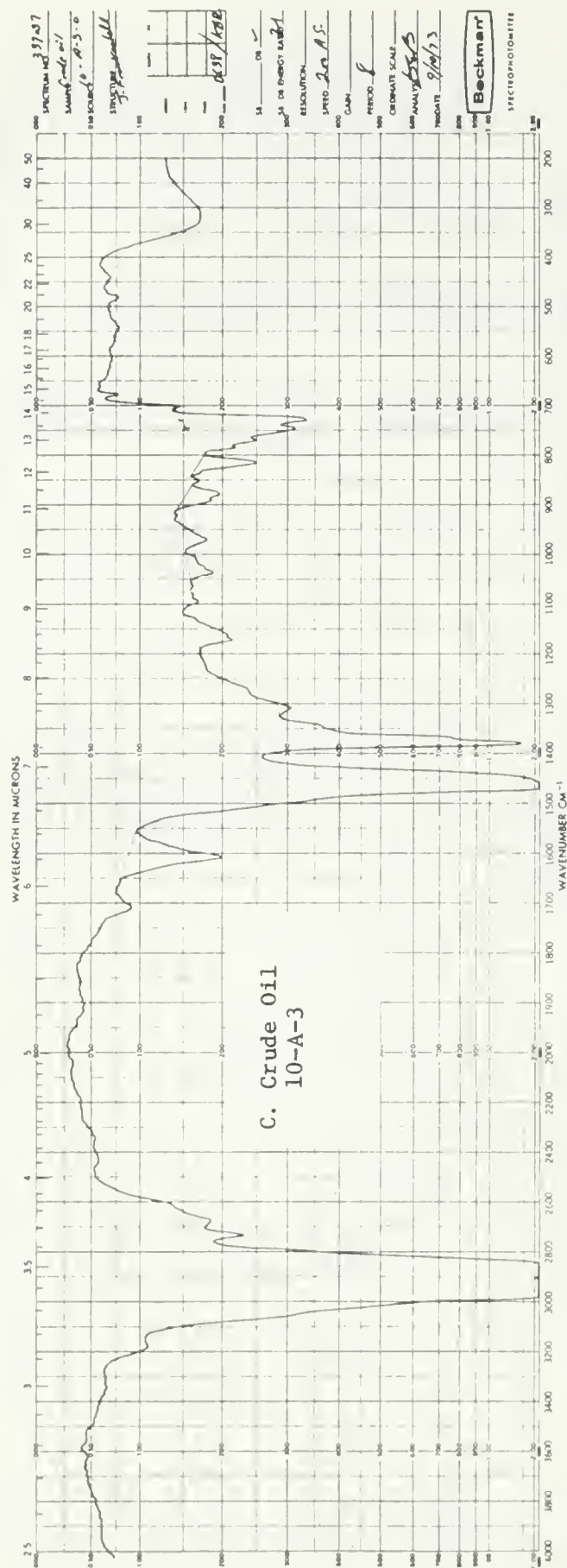


Figure 101. IR Spectra of Three Similar Commercial No. 2 Heating Oils

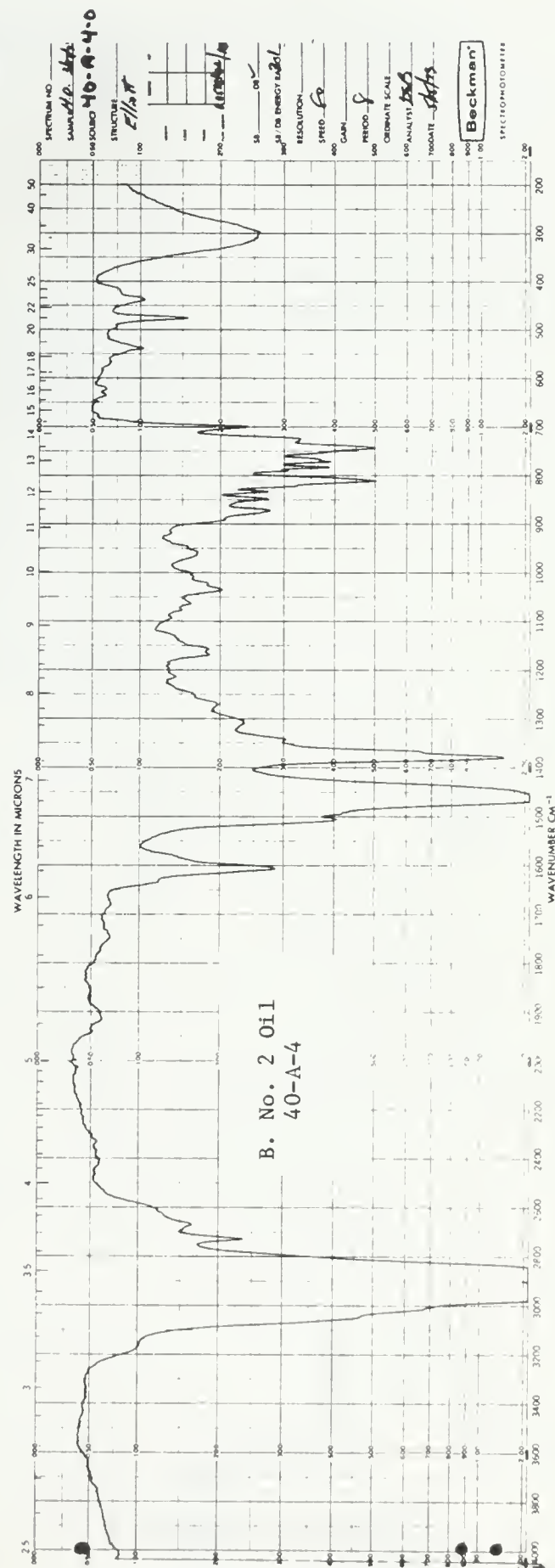
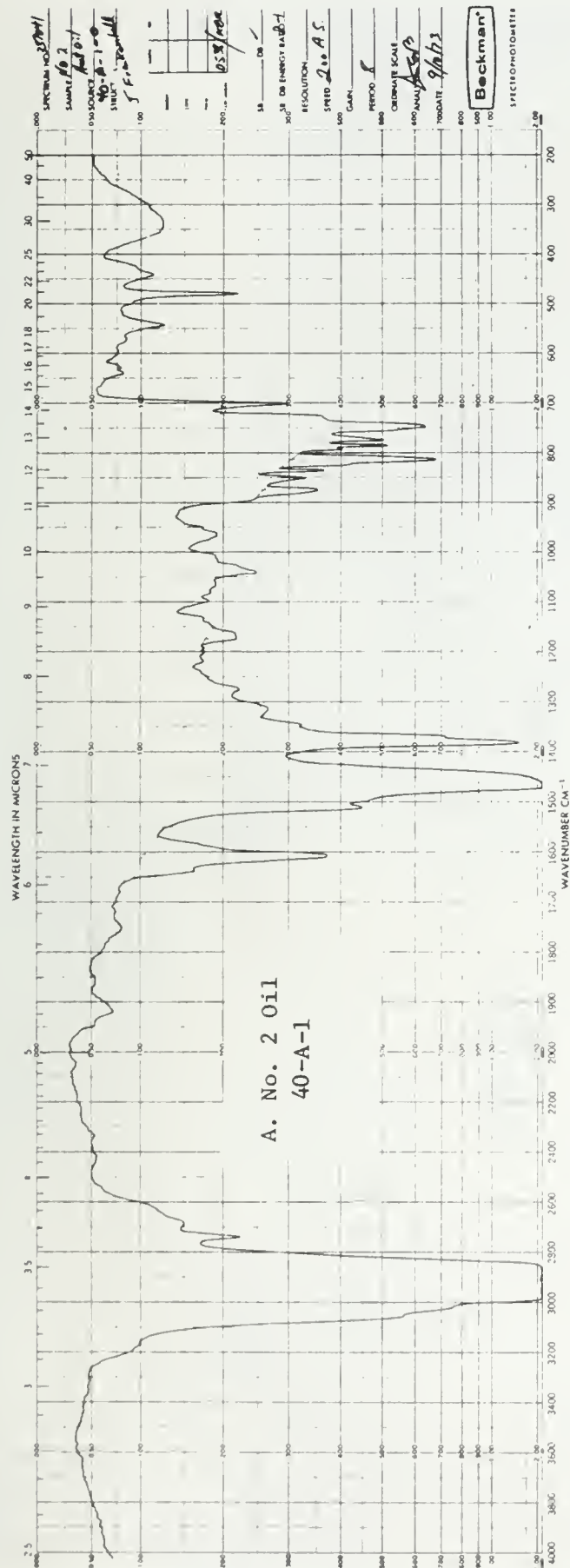


Figure 101. (Cont'd)

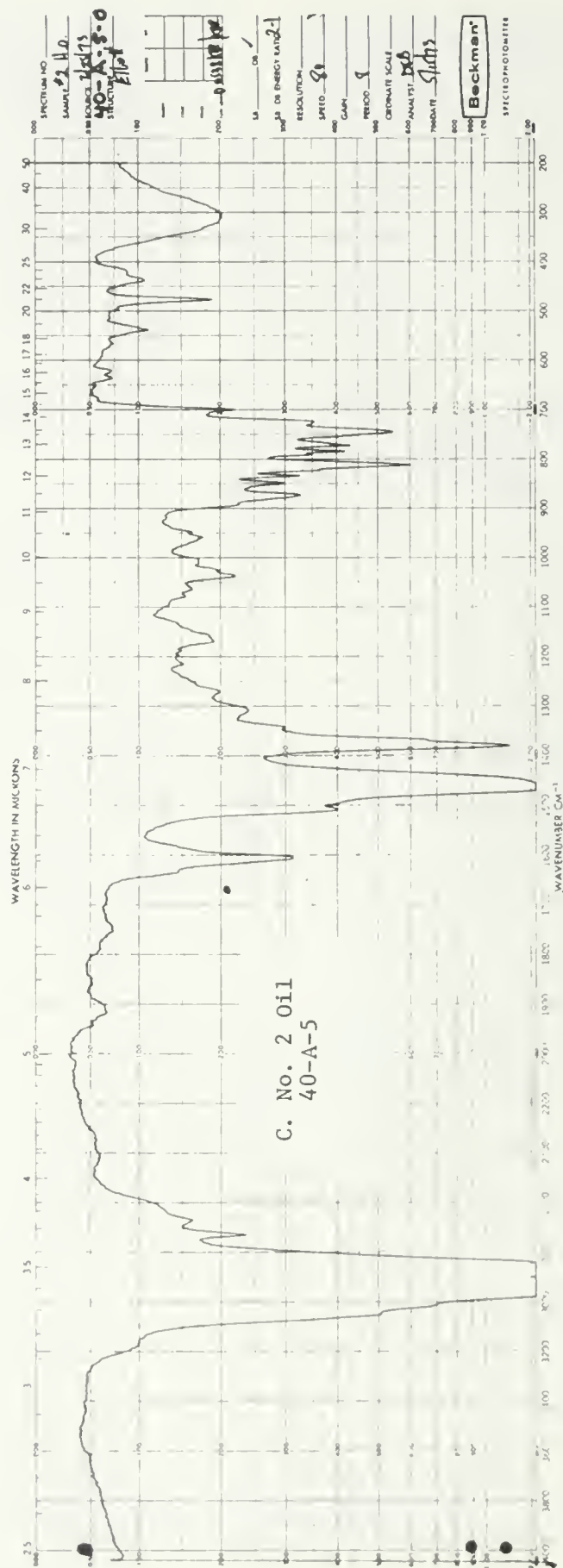


Figure 102. Liquid Chromatograms of No. 2 Heating Oils (RI Detector)

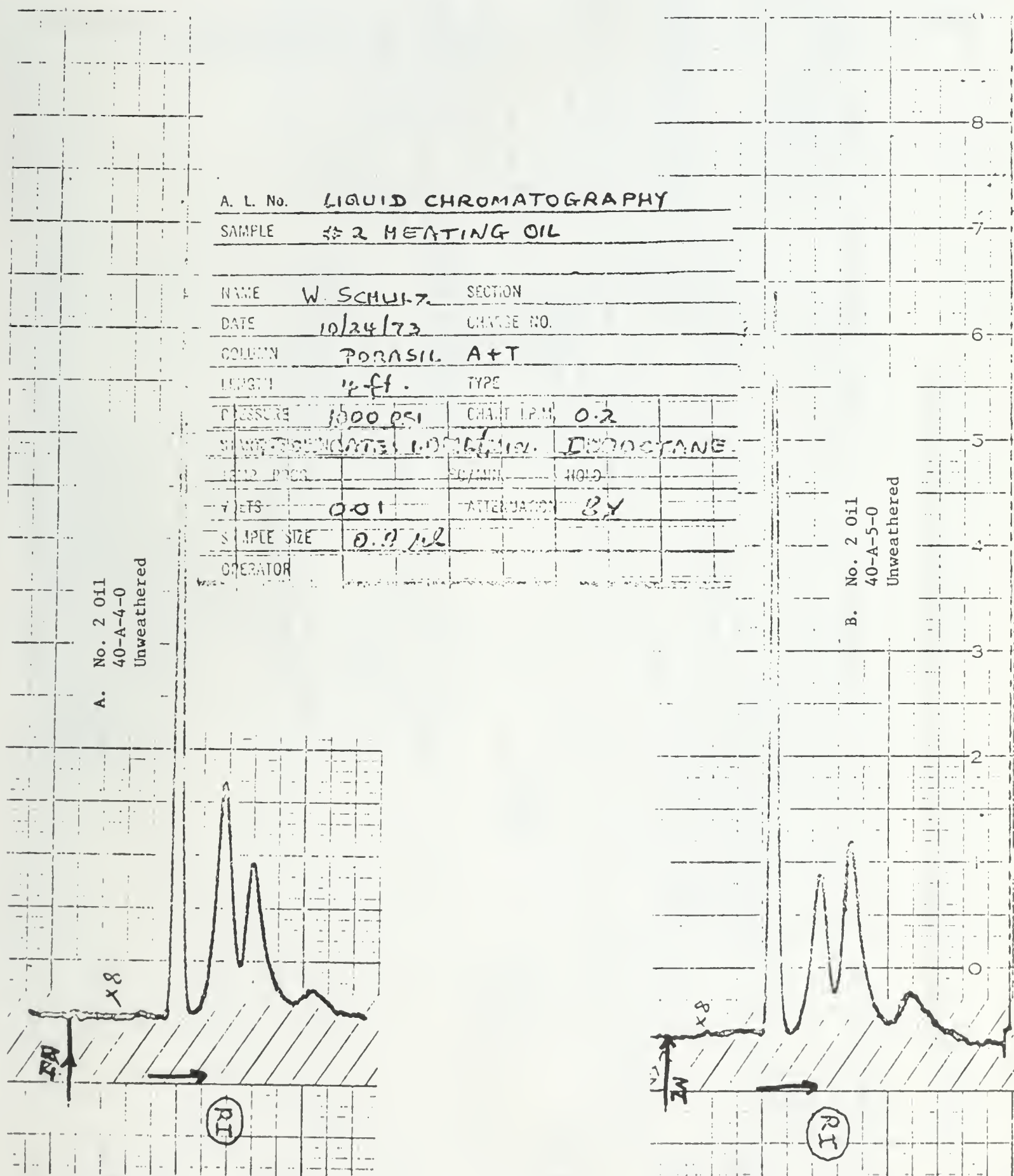


Figure 103. Liquid Chromatograms of No. 2 Heating Oils (UV-Detection)

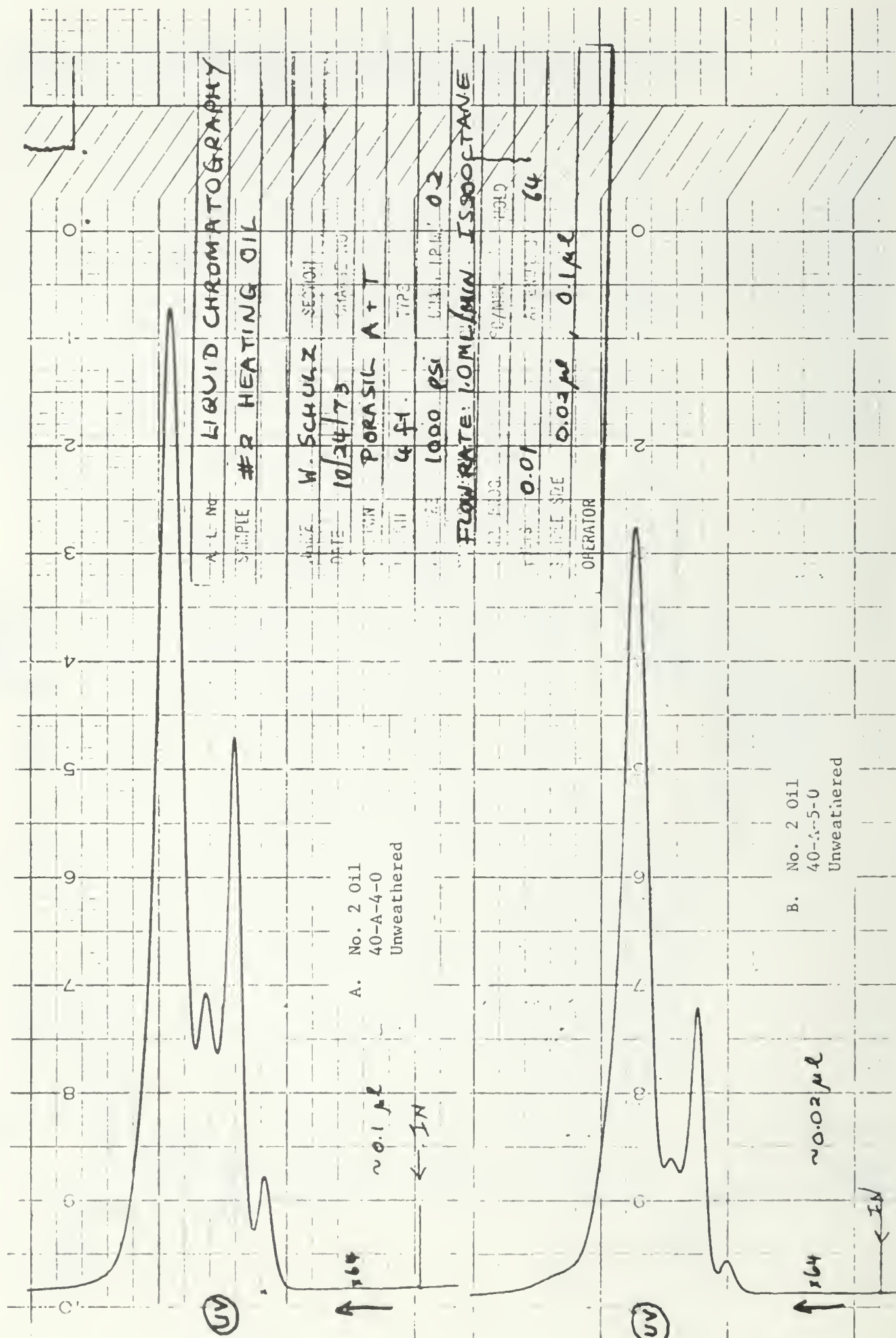


Figure 104. Liquid Chromatogram of No. 2 Oil 40-A-1 (Both UV and RI Detection)

LIQUID CHROMATOGRAPHY			
A. L. NO.	337041		
SAMPLE	#2 HEATING OIL		
	40-A-1-O		
NAME	FRANKENFELD SECTION		
DATE	10/18/73		
COLEMAN	PODASIL A+T		
DEPTH	4 ft. TYPE		
PRESSURE	1000 PSI	CHART 1 IN.	0.2
FLOW RATE: 1.0 ML/MIN ISOCTANES			
IF AP. PRESS.	50/100	HOLD	
VOLTS	0.01	ATTENUATION	
SAMPLE SIZE	0.1 μ l, 0.8 μ l		
OPERATOR			

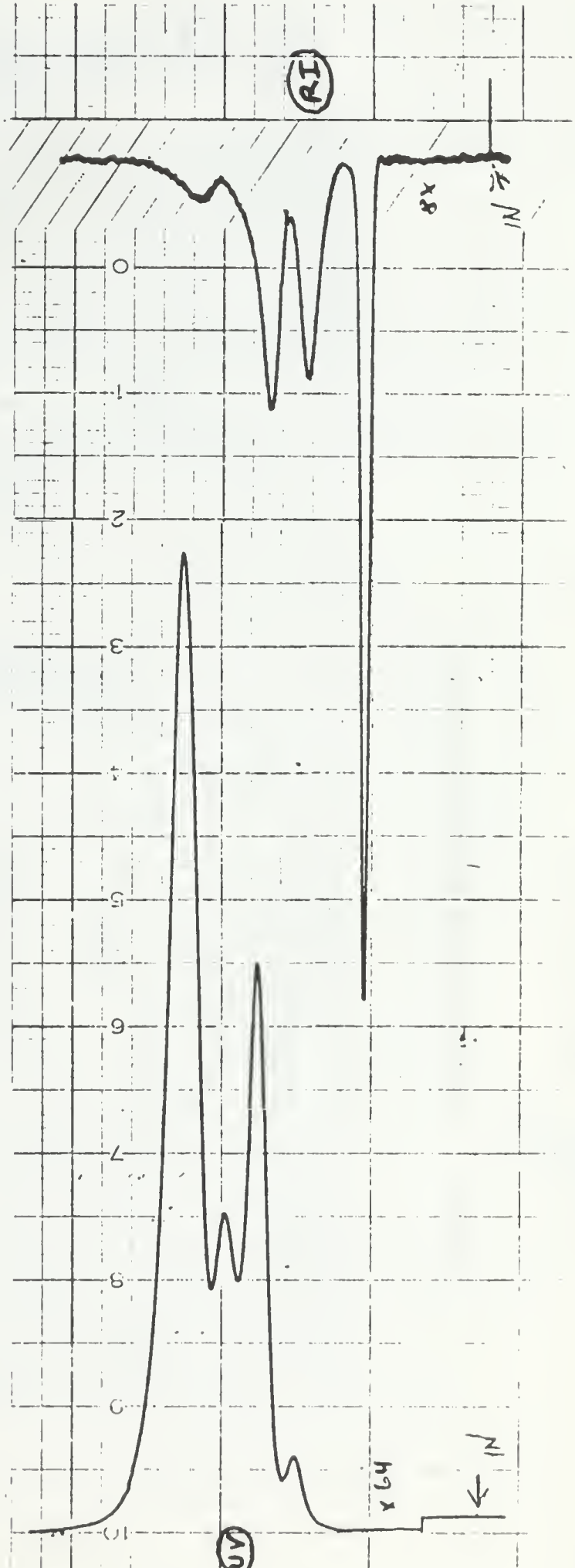


Figure 105. IR Spectra for Two Similar Residual Fuels

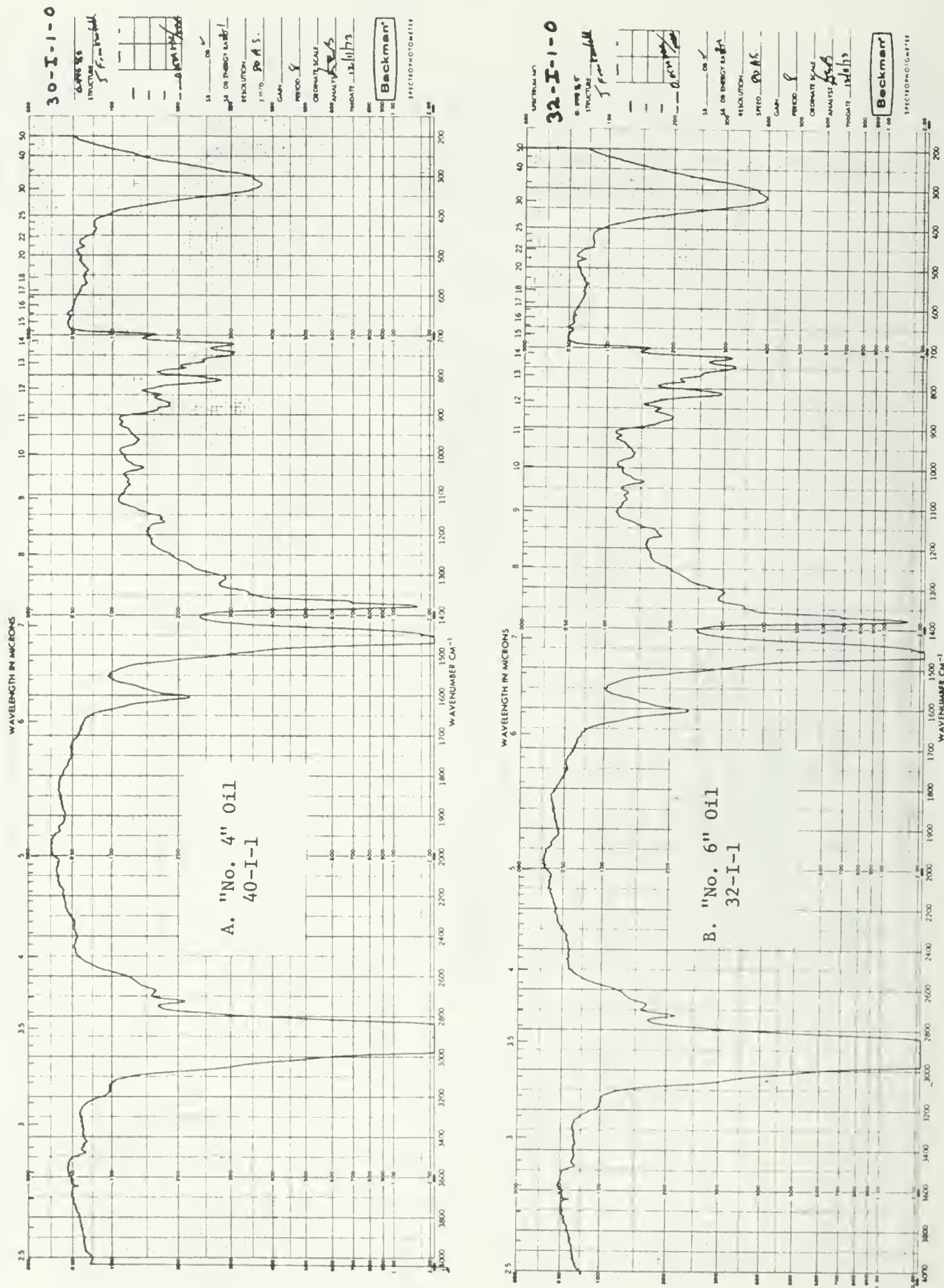


Figure 106. Liquid Chromatogram of
"No. 4" Oil
30-I-1

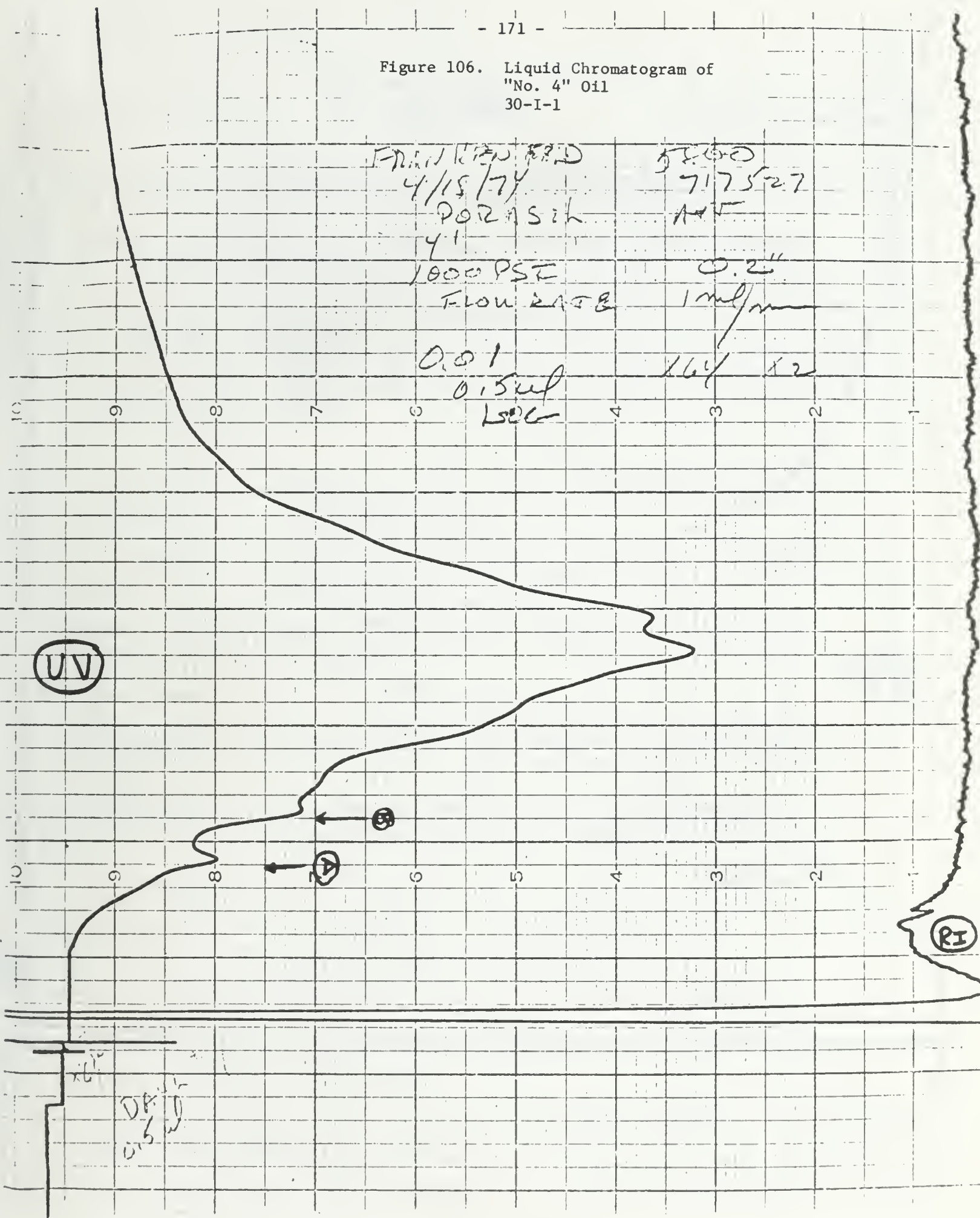


Figure 107. Liquid Chromatogram of
"No. 6" Oil
32-I-1

F.2.6.11/11/22 W 5.800
4/15/77 7/17-5-27
PORT-151L
4' 0 4
1000 PSI 0.2"
FLAN RATE 1 ml/min
0.01 UV RI
0.5 ul X44 X2
W.C.

UV

RI

8

7

1.6
5.1

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35. W. W. Schulz Exxon Research and Engineering Co., unpublished research.
36. J. W. Frankenfeld, J. Chromatography, 18, 179 (1965).
37. Samples and comments concerning G.C. traces were kindly furnished by Dr. A. P. Bentz, U.S.C.G. R&D Labs., Groton, Conn., the contract technical monitor.

APPENDIX A

Procedure for Sample Handling and Analyses

A. Sample Work-Up

The spill sample is divided into approximately 10cc portions and centrifuged in a small bench-top centrifuge for 10 minutes at 6000 rpm. The upper, oily layer is drawn off by pipette and stored in stoppered, brown bottles or vials under a blanket of nitrogen. At this point visual observations should be recorded. These should include color, clarity, viscosity, degree of emulsification and any unusual properties noted. The samples are then delivered to the appropriate laboratories for analysis.

B. Thin Layer Chromatography^a

One drop of the test oil is dissolved in about one cc of high grade n-hexane. About 10 microliters of the mixture is spotted, 1 cm from the bottom, on a 20cm x 20cm TLC plate coated with a 0.2mm layer of silica gel F-254 or 60-F.^b Side-by-side on a ruled line are spotted similar concentrations of standard solutions each of the suspect classes of petroleum products. The plate is developed with a mixture of high purity n-hexane and glacial acetic acid (50:1) in an ascending manner for 15 cm in a closed but unsaturated TLC chamber. The plate is removed and air-dried for 10-15 minutes at room temperature or for shorter periods in an oven. The dry plate is visualized first under long wavelength (3600Å) UV light and the spots or zones marked on the plate or described in a notebook. The procedure is repeated on the same plate with short wave (2500Å) UV light.^c The plate is exposed to iodine vapors in a closed chamber (glass TLC development chamber will do) for 15 min to several hours (hood). The spots are again marked or photographed. The plate is removed from the iodine chamber and allowed to weather in the hood until the spots fade.^d Finally the plate is sprayed lightly with H₂SO₄-Na₂Cr₂O₇ (ordinary laboratory cleaning solution), allowed to air dry a few minutes and then charred in an oven for 1/2 to 1-1/2 hrs at 120°C. This affords a permanent record.

If a lube oil or No. 2 fuel oil is suspected, it is best to repeat the above procedure using an eluting solvent richer in acetic acid (hexane: HOAc; 30:1).

- - - - -

- a. Conditions are suggested as starting points only; each laboratory should work out its own standard procedures. The plates do not need to be activated but should be stored in desiccators over drying agent after the box is opened.
- b. Suppliers include SGA Scientific Inc., Bloomfield, N.J.; EM Laboratories Inc. 500 Exec. Blvd., Elmsford, N.Y. and Analtech Inc., Wilmington, Del.
- c. The spots may be photographed using Polaroid type 108 film. Long exposure times (10-15 min) are required.
- d. Time can be saved if two or more plates are used at the beginning so that various visualization techniques can be used simultaneously.

C. Gas Chromatographic Analysis

If the centrifuged sample is fluid, the oil can be injected neat. If extremely viscous, the sample should be shaken with hexane or pentane, allowed to settle and the solution injected. If the sample is injected neat 0.5-1.5 microliter is used. About 5-10 microliters of solutions are employed. The instrument should be a Perkin-Elmer Model 900 gas chromatograph or equivalent, fitted with a flame ionization detector. The column is 15', 1/8" stainless steel packed with 3% SE-30 on Supelcoport*. Typical conditions are as follows:

Gas flow rates: 30/30 cc/min
Temperatures: Block, 300°C; Injection port, 300°C
Column Temp.: Start, 60°C; final 350°C
Program Rate: 8°/min

Suspect pollution sources, preferably artificially weathered, should be run, directly after the spill sample, under the same conditions.

D. Measurement of GC Peak Ratios

The most useful peaks for identification purposes are those occurring at about 17.2 min (n-C₁₇), 17.4 min (pristane), 18.6 min. (n-C₁₈) and 18.8 min (phytane) retention times under the above column conditions. The peak heights are determined by measuring a line from the apex of the peak to a line tangential to the two closest minimum points. This is illustrated in Figure A1. The values are ratioed. Recommended ratios:

$\frac{\text{pristane}}{\text{phytane}}$	$\frac{\text{n-C}_{17}}{\text{pristane}}$	$\frac{\text{n-C}_{18}}{\text{phytane}}$
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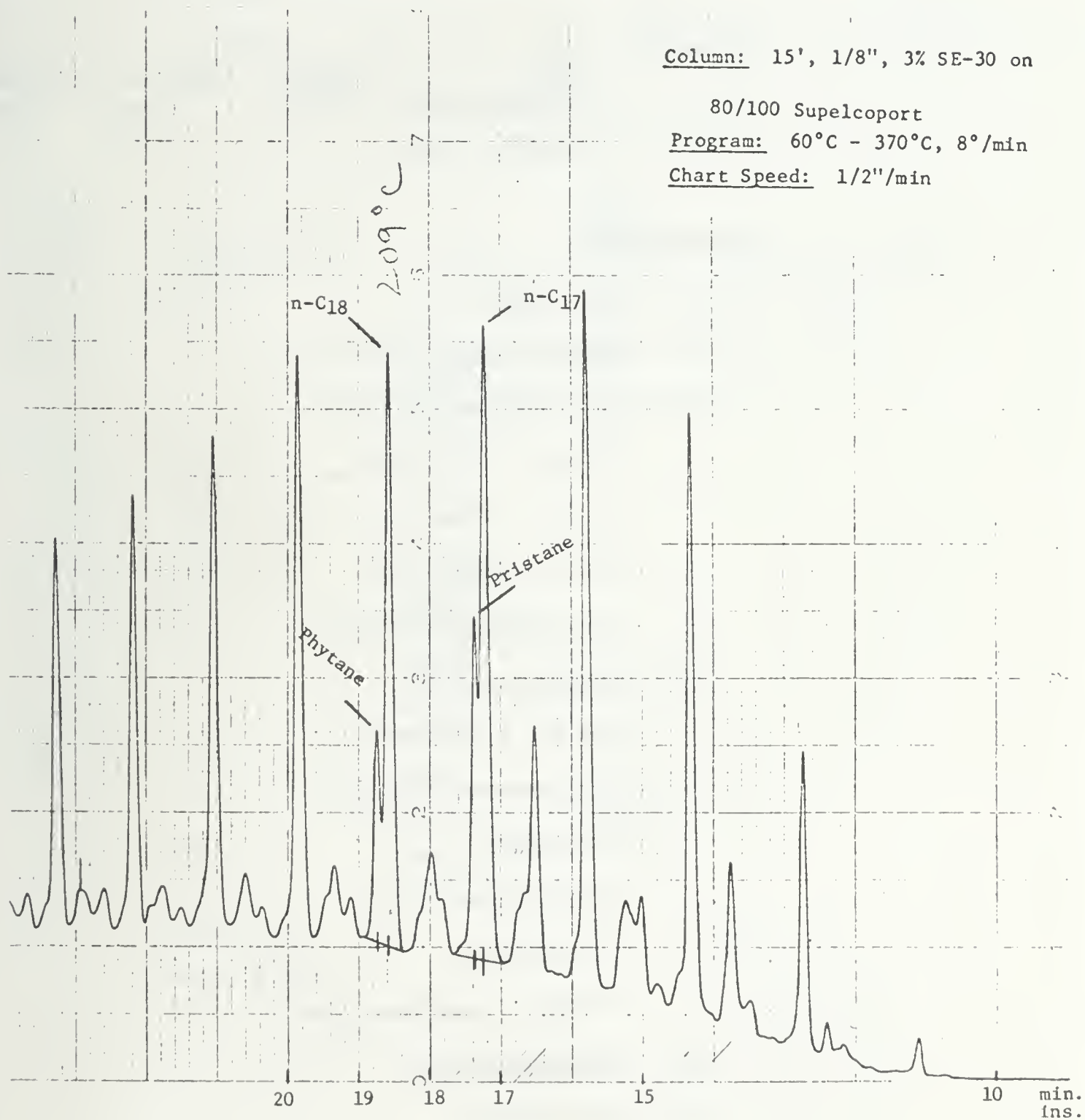
E. Infrared Analysis

The instrument employed should be a Beckman IR 12 or equivalent. If the original spill sample, after centrifuging, is fluid, the spectrum should be run in a fixed path length KBr cell, approximately 0.05 mm. If the oil is too viscous to fill the cell conveniently, it should be smeared between two polished salt plates fitted with a 0.05 mm spacer. The spectrum is run for the entire range of wavelengths, 2.5 μ - 5.0 μ (200-4000 cm⁻¹). Artificially weathered, authentic samples of suspect sources should be analyzed under similar conditions for comparison.

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* Supelco Inc., Supelco Park, Bellefonte, Pa. 16823.

Figure A-1. Illustration of GC Peak Ratio Method
(Crude Oil 10-A-2)



APPENDIX B

EXPLANATION OF CODING SYSTEM FOR
TEST SAMPLES

The code system to be employed in this study is as follows:

Sample No.:	10	-	A	-	1	-	I
	Oil		Company		Individual		Weathering
	Category		Code		Sample		History
					No.		

Category Code

10 = Crude Oils

20 = Residual Fuels (Bunker C)

30 = Blended Residual Fuels

30 = No. 4 Fuel Oil

31 = No. 5 Fuel Oil

32 = No. 6 Fuel Oil

33 = Navy Special Fuel

40 = Distillate Fuels

40 = No. 2 Heating Oil

41 = Kerosene a Gas Oil

42 = Diesel

43 = Jet Fuel

44 = Gasoline

45 = Navy Distillate Fuel

50 = Lubricating Oils

60 = Miscellaneous

60 = White Oils

61 = Outboard Motor Oil

Weathering History Code

0 = Unweathered

I = 24 Hours

II = 7 Days

III = 14 Days

APPENDIX TABLE B1

SAMPLES PROCURED

<u>Sample Number</u>	<u>Category</u>	<u>Origin</u>	<u>API Gravity (60°F)</u>	<u>Characteristics¹</u>
10-A-1	Crude Oil	Venezuela	18.0	Heavy, Aromatic
10-A-2	" "	Libya	41.4	Light Paraffinic
10-A-3	" "	Louisiana (off shore)	31.9	Aromatic, Medium
10-A-4	" "	Venezuela	24.1	
10-A-5	" "	Algeria		
10-A-6	" "	Ecuador		
10-A-7	" "	Indonesia		
10-A-8	" "	Denmark (North Sea)		
10-A-9	" "	Arabia		
10-A-10	" "	Nigeria		
10-A-11	" "	Libya	44.2	
10-A-12	" "	Texas	27.9	
10-A-13	" "	Louisiana	29.2	
10-A-14	" "	Texas		
10-B-1	" "	Qatar		
20-A-1	Resid. Fuel			Bunker "C"
30-A-1	Blended Resid.			No. 4 Fuel Oil
30-F-1	" "			No. 4 Fuel Oil
30-I-1	" "			No. 4 Fuel Oil
31-A-1	" "			No. 5 Fuel Oil
31-F-1	" "			No. 5 Fuel Oil
31-F-2	" "			No. 5 Fuel Oil
31-F-3	" "			No. 5 Fuel Oil

APPENDIX B (CONTD)

<u>Sample Number</u>	<u>Category</u>	<u>Origin</u>	<u>API Gravity (60°F)</u>	<u>Characteristics</u>
32-A-1	" "			Low Sulfur No. 6
32-A-2	" "			Med. Sulfur No. 6
32-F-1	" "			No. 6 Fuel Oil
32-F-2	" "			No. 6 Fuel Oil
32-H-1	" "			No. 6 Fuel Oil
33-X-1	Blended Resid			Navy Special Fuel
40-A-1	Distillate Fuels			No. 2 Heating Oil
40-A-2	" "			No. 2 Heating Oil
40-A-3	" "			No. 2 Heating Oil
40-A-4	" "			No. 2 Heating Oil
40-A-5	" "			No. 2 Heating Oil
40-B-1	" "			No. 2 Heating Oil
40-F-1	" "			No. 2 Heating Oil
40-H-1	" "			No. 2 Heating Oil
41-A-1	" "			Marine Gas Oil
42-A-1	" "			Automotive Diesel
42-A-2	" "			Automotive Diesel
42-A-3	" "			Marine Diesel
43-A-1	" "			Jet Fuel A-1
45-X-1	" "			Navy Distillate Fuel
46-A-1	" "			Premium Gasoline
50-A-1	Lubricating Oils			Multigrade
50-A-2	" "			Multigrade
50-C-1	" "			SAE 30
50-C-2	" "			Multigrade
50-D-1	" "			SAE 20
50-D-2	" "			
50-F-1	" "			SAE 20
50-F-2	" "			Multigrade
50-G-1	" "			SAE 30
50-G-2	" "			Multigrade
60-X-1	Miscellaneous			White Oil
60-X-2	Miscellaneous			White Oil
60-X-3	Miscellaneous			Outboard Motor Oil

APPENDIX C

DATA FOR LABORATORY WEATHERING TRIALS

TABLE C-1

PETROLEUM PRODUCTS USED IN FIRST
SET OF SIMULATED WEATHERING EXPERIMENTS

Average Temp. for Period: 85°F

<u>Simulator</u>	<u>Code No.</u>	<u>Type of Oil</u>
1	10-A-3	Crude
2	40-A-1	No. 2 Heating Oil
3	20-A-1	Bunker "C"
4	42-A-1	Automotive Diesel
5	10-A-2	Crude
6	60-X-2	White Oil
7	50-A-1	Multigrade Lube Oil

TABLE C-2

OILS USED IN SECOND SERIES
OF WEATHERING EXPERIMENTS

Average Temp. for Period: 75°F

<u>Simulator</u>	<u>Code No.</u>	<u>Type of Oil</u>
1	10-A-1	Crude
2	40-A-2	No. 2 Heating Oil
3	10-A-4	Crude
4	41-A-1	Marine Diesel
5	10-B-1	Crude
6	33-X-1	Navy Special
7	50-C-1	Multigrade Lube
8	50-F-1	SAE 20 Lube
9	30-A-1	No. 4 Oil
10	45-X-1	Navy Distillate Fuel

TABLE C-3

Petroleum Products Used in Third
Series of Weathering Experiments

Average Temp. for Period: 65°F

<u>Simulator</u>	<u>Code No.</u>	<u>Type of Oil</u>
1	10-A-5	Crude Oil
2	40-A-3	No. 2 Heating Oil
3	10-A-14	Crude Oil
4	42-A-2	Automotive Diesel
5	31-A-1	No. 5 Fuel Oil
6	32-A-1	No. 6 Fuel Oil
7	50-A-2	Multigrade Lube Oil
8	10-A-8	Crude Oil
9*	46-A-1	Premium Gasoline
10*	43-A-1	Jet Fuel "A"

* No weathered samples could be obtained due to extreme volatility of material.

TABLE C-4

Oils Used in Fourth Series
of Weathering Experiments

Average Temp. for Period: 73°F

<u>Simulator</u>	<u>Code No.</u>	<u>Type of Oil</u>
1	32-A-2	No. 6 Fuel Oil
2	42-A-3	Marine Diesel
3	10-A-6	Crude Oil
4	10-A-9	Crude Oil
5	10-A-10	Crude Oil
6	10-A-7	Crude Oil
7	60-X-1	White Oil
8	50-C-2	Multigrade Lube Oil
9	50-D-2	Lube Oil
10	50-D-1	SAE 20 Lube Oil

TABLE C-5

Petroleum Products Used in the Fifth
Set of Weathering Experiments

Average Temp. for Period: 74°F

<u>Simulator</u>	<u>Code No.</u>	<u>Type of Oil</u>
1	50-F-2	Multigrade Lube Oil
2	50-G-2	Multigrade Lube Oil
3	60-X-3	Outboard Motor Oil
4	42-F-1	No. 2 Heating Oil
5	42-H-1	No. 2 Heating Oil
6	42-B-1	No. 2 Heating Oil
7	31-F-1	No. 5 Oil
8	31-F-2	No. 5 Oil
9	32-F-1	No. 6 Oil
10	32-H-1	No. 6 Oil

TABLE C-6

Petroleum Products Used in the Sixth
Set of Weathering Experiments

Average Temp. for Period: 73°F

<u>Simulator</u>	<u>Code No.</u>	<u>Type of Oil</u>
1	10-A-11	Crude Oil
2	10-A-12	Crude Oil
3	10-A-13	Crude Oil
4	32-F-2	No. 6 Oil
5	31-F-3	No. 5 Oil
6	30-F-1	No. 4 Oil
7	50-A-1*	Multigrade Lube Oil
8	33-X-1*	Navy Special Fuel
9	45-X-1*	Navy Distillate Fuel
10	50-G-1	SAE 30 Lube Oil

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* These are repeats of earlier runs.

APPENDIX TABLE D1

ANALYTICAL RESULTS

Specific Gravity Determinations

<u>Sample</u>	<u>Type of Oil</u>	<u>Weathering Time</u>	<u>Specific Gravity⁽¹⁾</u>
10-A-1-0	Crude	0	.9501
I		1 Day	.9708
II		1 Week	.9772
10-A-2-0	Crude	0	.8187
I		1 Day	.8723
II		1 Week	.8826
10-A-4-0	Crude	0	.9132
I		1 Day	.9427
II		1 Week	.9535
III		2 Weeks	.9532 ⁽²⁾
10-A-5-0	Crude	0	.8095
I		1 Day	.8746
II		1 Week	.8837
10-A-8-0	Crude	0	.8771
II		1 Week	.9250
10-A-14-0	Crude	0	.8594
I		1 Day	.9203
II		1 Week	.9326
10-B-1-0	Crude	0	.8194
I		1 Day	.8911
II		1 Week	.9035
III		2 Weeks	.9048
30-A-1-0	No. 4 Fuel Oil	0	.8731
I		1 Day	.8846
II		1 Week	.8854
III		2 Weeks	.8858 ⁽²⁾
31-A-1-0	No. 5 Fuel Oil	0	.8932
I		1 Day	.9001
II		1 Week	.9020
32-A-1-0	No. 6 Fuel Oil	0	.9030
I		1 Day	.9058
II		1 Week	.9070
33-X-1-0	"Navy Special" Fuel	0	.9155
I		1 Day	.9262
III		1 Week	.9371

APPENDIX D (Cont'd.)

<u>Sample</u>	<u>Type of Oil</u>	<u>Weathering Time</u>	<u>Specific Gravity⁽¹⁾</u>
40-A-2-0	No. 2 Heating Oil	0	.8669
I		1 Day	.8763
II		1 Week	.8848
III		2 Weeks	.8832
40-A-3-0	No. 2 Heating Oil	0	.8627
I		1 Day	.8768
II		1 Week	.8805
41-A-1-0	Marine Gas Oil	0	.8531
I		1 Day	.8513
II		1 Week	.8530
III		2 Weeks	.8504
42-A-1-0	Automotive Diesel	0	.8446
I		1 Day	.8474
42-A-2-0	Automotive Diesel	0	.8529
I		1 Day	.8576
II		1 Week	.8574
43-A-1-0	Jet Fuel A-1	0	.8147
I		1 Day	.8258
45-X-1-0	Navy Distillate Fuel	0	.8358
I		1 Day	.8389
II		1 Week	.8418
III		2 Weeks	.8410
46-A-1-0	Premium Gasoline	0	.7300
50-A-2-0	Lube Oil	0	.8795
I		1 Day	.8794
II		1 Week	.8794
50-C-1-0	Lube Oil	0	.8865
I		1 Day	.8857
II		1 Week	.8840
III		2 Weeks	.8843
50-F-1-0	Lube Oil	0	.8832
I		1 Day	.8813
II		1 Week	.8807
III		2 Weeks	.8796

(1) Avg. of two determinations unless otherwise noted.

(2) One sample only.

APPENDIX E

SCREENING OF SOLVENTS AND ADSORBENTS FOR TLC¹

<u>Coating²</u>	<u>Solvent System</u>	<u>Results</u>
SG	Ether	poor
SG	n-Hexane	good
SG	Hexane-trace HOAc	good
SG	Hexane: HOAc (50:1)	good
SG	Pet. ether	fair
SG	Pet. Ether-trace HOAc	fair
SG	Cyclohexane	fair
SG	Hexane: cyclohexane: HOAc (4:1:trace)	good
SG	Hexane: Benzene (4:1)	fair
SG	Benzene	poor
SG	CHCl ₃	poor
SG	CCl ₄	poor
SG	Benzene: Ethanol (4:1)	fair
SG	Methanol	poor
SG	Acetone	poor
Cellulose	Methanol	poor
Cellulose	Acetone	poor
SG-n-Hexadecane ³	Methanol	poor
	Methanol	poor
	CHCl ₃	poor
	Hexane-trace HOAc	fair
Alumina	Hexane-trace HOAc	fair
Alumina	Benzene	poor

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1. Test Oils (unweathered): two crudes, No. 2 fuel oil, Bunker "C" motor lubricant, white oil.
 2. SG = Silica gel 60F; Cellulose = Cellulose F; Alumina = Alumina GF.
 3. "Reversed phase" plates prepared by dipping silica gel plates in a 15% solution of hexadecane in ether for 20 seconds, then evaporating the solvent.

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